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THE MOLECULAR WEIGHT OF SULPHUR.

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The molecular weight of sulphur was first determined in 1832 by Dumas,[1] who made use of the vapor density method and apparatus now so well known by his name. The following table gives the results of this investigation:

Temperature.	Density.	Calculated for S_8.
506° C	6.512	6.644
493°	6.495	
524°	6.617	
524°	6.581	

This value for the molecular weight of sulphur (192) was so different from that which was naturally expected (64) from the general resemblance between sulphur and oxygen that it led Mitscherlich,[2] who was present when Dumas made his determinations, to repeat the work himself in the following year, with the result that he obtained the value 6.90 for the vapor density of sulphur at a temperature of 509° C., thus fully confirming Dumas' results.

[1] Ann. chim. phys. [2], **50**, 172. Obtained similar results in 1826 but did not publish them.

[2] Ann. Chem. (Liebig), **12**, 137; Ann. der phys., Pogg., **29**, 193.

It was not until 1860, twenty-seven years after, that the existence of molecules of sulphur containing two atoms (S_2) and corresponding to molecules of oxygen (O_2) was proved by Deville and Troost.[1] Using the Dumas method these chemists found the following values for the vapor density of sulphur:

Temperature.	Density.		Calculated for S_2.
860° C	2.28	2.22	2.22
	2.20	2.21	
	2.23	2.25	

Bineau[2] also claims to have obtained results which pointed to S_2 as the molecular formula of sulphur at about this time.

That the vapor density of sulphur is independent of the pressure was proved in 1878 by Troost,[3] who found the density at a temperature of 440° C. and a pressure of 104 mm. to be 6.7, while at the same temperature but at a pressure of 60 mm. 6.3 was the value obtained.

During the same year Victor and Carl Meyer,[4] using their new method of determining vapor densities, obtained a value 6.58 for the density of sulphur at a temperature which they vaguely describe as below red heat (Glühhitze) and in 1879 the same authors confirmed the results of Deville and Troost when they found the vapor density of sulphur to be 2.17 at yellow heat (Gelbhitze).

Pfaundler,[5] who about this time described a new method of determining vapor densities, states that, using his own apparatus, he had found satisfactory results for the vapor density of sulphur, which, presumably, means that he obtained values agreeing with S_6 as the molecular formula of this substance.

In 1882 Troost[6] again determined the vapor density of sulphur but this time at a temperature of 665° C. 2.92 and 2.94 were the values found at this temperature.

In 1888 Biltz,[7] at the suggestion of V. Meyer, undertook a very thorough investigation of the vapor density of sulphur at different temperatures, using both the apparatus of Dumas

[1] Ann. chim. phys. [3], **58**, 257.
[2] Compt. rend., **49**, 799. See also Ann. chim. phys. [3], **58**, 257, and **59**, 456.
[3] Compt. rend., **86**, 1396. [4] Ber. d. chem. Ges., **11**, 2259. and **12**, 1115.
[5] Ber. d. chem. Ges., **12**, 165. [6] Compt. rend., **95**, 30.
[7] Ztschr. phys. Chem., **3**, 920.

and that of V. Meyer for this purpose. He calls attention to the fact that the only determinations which lead to the acceptance of the molecular formula S_8 are those of Dumas and Mitscherlich and that these estimations were all made within a temperature interval of only 30°, an interval which he thinks is far from being sufficient to warrant the assumption of a second molecular formula. In the following table Biltz's results with the Dumas method[1] are presented :

Temperature.	Density.	Molecular weight.	No. of atoms in molecule.
467.9° C.	7.937	229.2	7.16
480.5	7.448	215.1	6.72
487.4	7.301	210.9	6.59
501.7	7.015	202.6	6.33
518.0	7.036	203.2	6.35
523.6	7.086	204.6	6.40
534.4	6.975	201.4	6.29
580.9	5.509	159.1	4.97
606.0	4.734	136.7	4.27

From these results Biltz concludes that the only molecules of sulphur capable of existing in the gaseous state are those corresponding to the formula S_2, and these only at higher temperatures. At lower temperatures almost any desired greater value may be obtained for the density leading to the arbitrary assumption of molecules S_8, S_7, or in general S_n. Only the value corresponding to the molecule S_2 is constant within a considerable range of temperature and hence it alone should be taken into consideration in deciding the question of the molecular weight of sulphur.

To these conclusions of Biltz, W. Ramsay[2] takes exception and ventures the assertion that they are not entirely justified by the facts. According to him it is by no means proved that molecules corresponding to the formula S_8 do not exist. The results of Biltz simply lead one to suspect that perhaps more complex molecules, possibly S_6 or S_{10} may exist.

Paterno and Nasini[3] in 1888 determined the molecular weight of sulphur in benzene by the freezing-point method,

[1] The results with the Meyer apparatus are not here given as they are not so reliable as those made by the Dumas method.

[2] Ztschr. phys. Chem., **3**, 67. See in this connection Biltz's answer, Ztschr. phys. Chem., **3**, 228.

[3] Ber. d. chem. Ges., **21**, 2153.

obtaining results which led them to conclude that the molecular weight of sulphur in this solvent was 192 and that molecules having the formula S_8 really do exist.

During the next year (1889) Biltz and Meyer[1] determined the vapor density of sulphur at 1719° C. and found even at this high temperature results agreeing closely with the formula S_2.

Beckmann[2] in 1890 was the first to make use of the boiling-point method for determining the molecular weight of sulphur. He confirms Biltz's statement that but little value can be attached to the results of Paterno and Nasini on account of the slight solubility of sulphur in this liquid. Using carbon disulphide as a solvent he obtained values varying from 247 to 314, according to the concentration, for the molecular weight of sulphur and states that these values are very near that required by the formula S_8 (256). He, however, regards these results as only approximate and suggests the use of other solvents, particularly of sulphur chloride, to decide this question of the true molecular weight of sulphur.[3] He then calls attention to the fact that Biltz's determinations of the vapor density of sulphur at a temperature (468° C.) slightly above its boiling-point do not exclude the possibility of the existence of molecules S_8 at the boiling-point (448° C.) of sulphur.

Acting apparently on a suggestion of Ramsay, C. Schall[4] in 1890 determined the vapor density of sulphur under diminished pressure in the vapor of boiling diphenylamine and phenanthrene. According to this investigator the values obtained in phenanthrene vapor (boiling-point about 340° C.) though they differ considerably from each other (6.34–7.60), seem to indicate the correctness of Biltz's inference, according to which trimolecular sulphur (S_6) does not exist. On the other hand, the remarkably constant results found for the density of sulphur in the vapor of diphenylamine (boiling-point 300° C.), appear to favor the assumption of the existence of tetramolecular sulphur (S_8), near the boiling-point of

[1] Ztschr. phys. Chem., **4**, 266. [2] Ztschr. phys. Chem., **5**, 80.

[3] Perhaps it should be noted here that these determinations of the molecular weight of sulphur were among the first made by Beckmann by this method.

[4] Ber. d. chem. Ges., **23**, 1704.

this substance as Beckmann has already shown by the boiling-point method.

E. Riecke[1] regards the decreasing vapor density of sulphur with rise of temperature as a case of dissociation by steps, (stufenweise Dissociation), of molecules S_8 to S_2 and S_6 and that finally S_8 breaks up into three molecules of S_2. According to this author both Beckmann and Schall have shown that sulphur molecules of the formula S_8 exist and the investigations of Biltz make it probable that on vaporizing sulphur at atmospheric pressure molecules S_8 are first evolved and that these split up into S_6 and S_2, and that in the further course of the dissociation the molecules S_6 also break up into three molecules of S_2. By making these and other assumptions he shows a certain coincidence between his calculated results and the values observed by Biltz for the vapor density of sulphur at different temperatures.

The molecular weight of sulphur was determined by J. Hertz[2] in naphthalene by the freezing-point method during the year 1890. His values varied from 262.3 to 279.4 according to the concentration and indicate a molecular weight of 256 for this substance. He also calls attention to the unsatisfactory results of the molecular weight determinations in benzene due to the slight solubility of sulphur in that solvent.

In 1892 Sakurai,[3] making use of an apparatus devised by himself, determined the molecular weight of sulphur in solution in carbon disulphide by the boiling-point method and obtained values varying from 252.3 to 254.9. He concludes from these results that the molecule of sulphur contains eight atoms (S_8).

Helff[4] in 1893 used both the boiling-point and freezing-point methods of determining molecular weights to solve the question as to the molecular weight of sulphur. In carbon disulphide he found values from 258 to 343 according to the concentration, while in melted phosphorus, the material used in the freezing-point method, his results varied from 234.6 to 251.1. Both methods, he states, indicate that the molecular weight of sulphur is 256 (S_8).

[1] Ztschr. phys. Chem., **6**, 430.
[2] Ztsch. phys. Chem., **6**, 358.
[3] J. Chem. Soc., **61**, 989.
[4] Ztschr. phys. Chem., **12**, 196.

A fourth method of determining molecular weights was used by G. Guglielmo[1] in 1892 to determine the molecular weight of sulphur. From the relative depressions of the vapor pressure which solutions in carbon disulphide show, and which for sufficiently dilute solutions of sulphur are constant, he finds that the molecule of sulphur contains eight or nine atoms according to the concentration.

It will naturally be thought by those reading this review of the very careful work done on the molecular weight of sulphur that the question is settled, that there can be no doubt that the molecular weight of this element at ordinary temperatures is 256 and that there are eight atoms in the sulphur molecule. It will be noted, however, that in none of these investigations has any attempt been made to show whether the two forms of sulphur known as the orthorhombic and monoclinic varieties have the same molecular weight. To be sure, the results in carbon disulphide may be regarded as determinations of the molecular weight of the orthorhombic modification, but no determinations exist of the molecular weight of the other form of sulphur. These two varieties of sulphur differ from each other not only in crystal form and color but also in specific gravity and melting-point so that it seemed *at first* not unlikely that these differences might be due to a difference in molecular weight of the two forms of sulphur.

It was found that sulphur crystallizes from boiling benzene and also from boiling toluene in beautiful transparent monoclinic needles, which, however, soon became opaque on standing from the transformation into the orthorhombic modification. It was naturally thought from this fact that it would be possible to determine the molecular weight of the monoclinic form of this substance by determining the molecular weight of sulphur in benzene and toluene at their boiling-points, since at these temperatures there is no longer any orthorhombic sulphur in solution. The following investigation was begun with this object in view, but the results obtained were so different from what was expected that the investigation was extended so as to include molecular weight determinations by both

[1] Real. Accad. Linc., 1892, **2**, 210-216.

the boiling- and freezing-point methods in a number of solvents.

Experimental.

Purification of the Sulphur.—Pure roll sulphur was first distilled in an atmosphere of carbon dioxide, rejecting both the first and last distillates and collecting only the middle portion. This middle fraction was again distilled in a stream of carbon dioxide, rejecting the end portions as before, and the middle distillate was then recrystallized several times from toluene in such a way that very small crystals were obtained. Toluene is a much better solvent for the purification of sulphur than carbon disulphide, as it is easily obtained pure and does not cling so tenaciously to the sulphur. The first and last portions of the recrystallized product were always rejected, the middle portion being washed with toluene to take out the mother liquor, drained and then washed with ether to remove the last traces of toluene and dried in the air. The purity of this material was proved by determining the amount of residue left after ignition and by analysis.

2.0241 grams sulphur gave on gentle ignition a residue of 0.0001 gram, corresponding to 0.005 per cent. of impurity.

Analyses by the Carius method, (heating the sulphur in a sealed tube with fuming nitric acid, precipitating and weighing the sulphuric acid formed as barium sulphate), gave the following results:[1]

I. 0.1771 gram sulphur gave 1.2932 grams $BaSO_4$.
II. 0.1833 " " " 1.3373 " "

	Gram sulphur taken.	Gram sulphur found.	Results in percentage.
I.	0.1771	0.17756	100.25
II.	0.1833	0.18362	100.17

$S = 32.06$. $BaSO_4 = 233.49$.

Determinations of the Molecular Weight of Sulphur by the Boiling-Point Method.

Apparatus and Method.—The apparatus used in the determination of the molecular weight by the boiling-point method was that recently described by Orndorff and Cameron.[2] The

[1] These analyses were made for us by Mr. D. A. Morton, an assistant in the laboratory, to whom we wish here to express our thanks.

[2] This JOURNAL, 17, 517.

thermometer was of the Beckmann differential type, made especially for us by Goetze, of Leipsic. It was graduated in hundredths of a degree, had a shorter, though wider, mercury bulb and larger capillary tube than the thermometers generally used in this work. The scale divisions were larger also, thus insuring greater accuracy in the readings. This thermometer was carefully calibrated on a dividing engine and found to have at no part of the scale an error of more than *one thousandth of a degree in one degree.* The readings were all made with a cathetometer located about two meters from the apparatus, and after every observation, care was taken to read the barometer also. In no case were the results calculated until the whole series of observations had been taken, thus avoiding prejudiced readings. No series has been omitted with the exception of two with benzene as a solvent and one with carbon disulphide. These determinations were made at the beginning of the work and before we thoroughly understood the method. In all other cases the results are given exactly as they were recorded. Whenever possible a series of determinations was made, as this method undoubtedly gives more accurate results. Where the individual values found for the molecular weights in a series do not differ very much from each other, the average of a series of determinations is given as well as the molecular weight at infinite dilution, and where two or more series of determinations are made the average of all the molecular weights at infinite dilution is stated. No corrections have been made for barometric changes or for errors in the thermometer, as these were in all cases *very* small and it was thought best to manipulate the results as little as possible. The solvents were in *all* cases carefully purified before being used. The boiling-points given for these substances were made with great care, using a standardized thermometer, entirely surrounded with the vapor of the boiling substance, to determine the temperature.

In representing the results by the graphic method we have in every case plotted the molecular weights as ordinates and the concentration, (number of grams of the solute in 100 grams of the solvent), as abscissas. This method is not only more accurate than that of plotting the molecular weights

against rises or depressions of temperature, as is usually done, but it is more rational, since what we wish to know is the *molecular weight at infinite dilution*. We have drawn a small circle around each point plotted and numbered it so that the reader may see at a glance what determinations belong together and just how much each determination is off its proper curve. The scales have been selected so as to exaggerate variations in molecular weights. Since the difference between the possible molecular weights is small (only 32), it is necessary to work with great care and in some cases to make several series of determinations in order to find the true molecular weight of sulphur.

In order to save time and also to avoid mistakes as far as possible, all the calculations were made on the Brunsviga calculating machine, which we highly recommend for this purpose.

Results with Toluene.—Toluene was the first solvent used by us in the determination of the molecular weight of sulphur by the boiling-point method. It is an ideal solvent for this purpose, as will be seen from the following results:

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent: *Toluene*.

Boiling-point 109.7° C. at 741.7 mm. barometric pressure.

Molecular elevation for 100 grams, 35°.

I.

	Grams solvent.	Grams substances.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight
1	78.04	0.6222	0.7973	0.097°	738.2	288
2	"	0.9071	1.1624	0.139	738.1	293
3	"	1.1973	1.5342	0.186	738.1	290
4	"	1.5570	1.9951	0.241	738.1	290
5	"	1.8748	2.4024	0.291	738.0	289
6	"	2.2023	2.8220	0.339	738.0	291
7	"	2.6102	3.3447	0.399	738.0	293

Barometer 738.2 — 738.0 mm. Average of series I **290.5**

Molecular weight at infinite dilution **288.5**

Molecular elevation at " " **34.9°**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight
8	79.68	0.4549	0.5709	0.071°	745.9	281
9	"	0.9950	1.2487	0.153	746.0	286
10	"	1.4584	1.8303	0.230	746.1	279
11	"	2.0134	2.5269	0.318	746.3	278
12	"	2.4814	3.1142	0.397	746.3	275
13	"	2.9432	3.6938	0.468	746.4	276
14	"	3.4002	4.2673	0.536	746.4	279
15	"	4.0384	5.0683	0.631	746.5	281

Barometer 745.8 — 746.5 mm. Average of series II 279.3

Molecular weight at infinite dilution 282.0

Molecular elevation at " " 35.7°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
16	84.28	0.4371	0.5186	0.064°	738.0	284
17	"	0.9141	1.0846	0.130	738.1	292
18	"	1.3505	2.6024	0.194	738.2	289
19	"	1.8316	2.1732	0.263	738.2	289
20	"	2.3864	2.8315	0.348	738.3	285
21	"	2.8386	3.3681	0.424	738.4	278
22	"	3.4993	4.1520	0.518	738.6	281
23	"	4.1804	4.9601	0.625	738.7	278

Barometer 738.0 — 738.7 mm. Average of series III 284.5

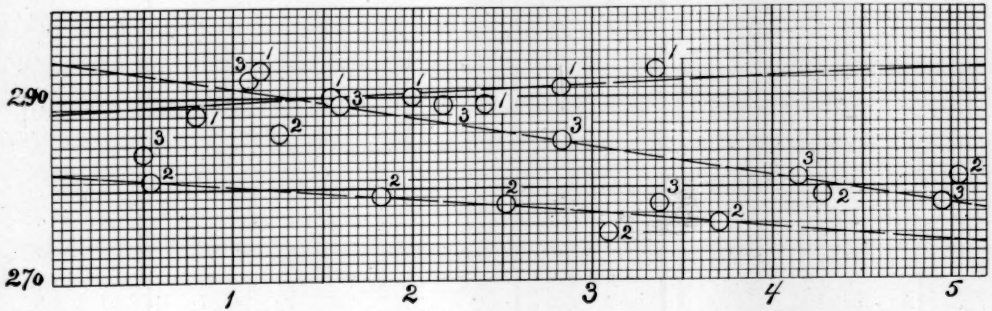
Molecular weight at infinite dilution 294.0

Molecular elevation at " " 34.3°

Average of 23 determinations in toluene 284.7

Average of molecular weights at infinite dilution 288.1

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Toluene by the Boiling-Point Method.



These results certainly indicate that the molecular weight of sulphur is 288 and that its molecular formula is S_8.

Results with Carbon Disulphide.—As the molecular weight of sulphur in carbon disulphide has been determined by Beckmann, Sakurai and Helff, and each obtained values approximating 256 (S_8), we were at first inclined to ascribe the difference between our results in toluene and those of these investigators in carbon disulphide to the fact that our results gave the molecular weight of monoclinic sulphur, while those of the others represented the molecular weight of the orthorhombic variety. It seemed hardly possible, however, that the monoclinic sulphur should have a different molecular weight from that of the orthorhombic form and still less probable that it should have a *higher* molecular weight than the other variety, which is the stable modification at ordinary temperatures. We therefore concluded to repeat the work with carbon disulphide. It was soon found that this solvent was by no means so easy to work with as toluene. In order to avoid errors of readings and to get results that agreed with each other, we added at first a large amount of sulphur. After this was done no further difficulty was experienced in getting good readings with this solvent. The introduction of sulphur seemed to make the boiling more uniform and the large amount of sulphur used at first gave a considerable rise of temperature, so that errors in the readings, (which are always greater in the first observations), affected the final results very little. As will be seen from the results the molecular weight increases but slightly with increasing concentration, so that this method gives accurate values for the molecular weight of sulphur.

The following are the results in tabular form:

SULPHUR,

$S_8 = 256$; $S_8 = 288$.

Solvent: *Carbon Disulphide.*
Boiling-point 46.0° C. at 757.4 mm. barometric pressure.
Molecular elevation for 100 grams, 23.75°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	123.70	4.1565	3.3601	0.271°	751.4	294
2	"	6.1128	4.9416	0.419	751.5	280
3	"	7.0244	5.6786	0.481	751.6	280

Barometer 751.1 — 751.6 mm. Average of series I **284.6**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
4	113.68	5.3530	4.7088	0.378°	757.1	296
5	"	7.2579	6.3845	0.518	757.0	293
6	"	9.1103	8.0140	0.650	757.0	293
7	"	11.0012	9.6773	0.781	756.9	294
8	"	13.0693	11.4966	0.928	756.8	294
9	"	15.2140	13.3832	1.070	756.7	297

Barometer 757.4 — 756.7 mm. Average of series II **294.5**

Molecular weight at infinite dilution **289.0**

Molecular elevation at " " **23.7°**

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
10	119.03	8.9310	7.5032	0.595°	753.9	299
11	"	10.7175	9.0040	0.716	753.9	299
12	"	12.5151	10.5142	0.840	753.9	297
13	"	14.3147	12.0261	0.950	753.8	301
14	"	15.7343	13.2188	1.041	753.7	302

Barometer 754.1 — 753.7 mm. Average of series III **299.6**

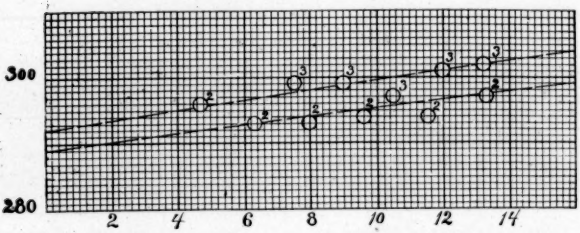
Molecular weight at infinite dilution **292.0**

Molecular elevation at " " **23.5°**

Average of 14 determinations in carbon disulphide **292.9**

Average of molecular weights at infinite dilution **290.5**

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Carbon Disulphide by the Boiling-Point Method.



These results, like those obtained with toluene as a solvent indicate that the molecular weight of sulphur is 288, and that there are nine atoms in the molecule. They also show that both the orthorhombic and monoclinic varieties of sulphur have the same molecular weight.

Results with Benzene.—As the determinations with toluene and carbon disulphide led to conclusions so different from those made by other investigators and referred to above, it was thought advisable to make further molecular weight determinations by this method, using other solvents. Benzene was the the next solvent selected. Sulphur is not very soluble in this liquid, however, even at the boiling-point, and for that reason the results are not quite so satisfactory as those with toluene and carbon disulphide. The change of the molecular weight with increase of concentration is quite rapid, so that here only the molecular weight at infinite dilution is to be considered.

The following table gives the results found :

SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent : *Benzene*.
Boiling-point 79.6° at 744.3 mm. barometric pressure.
Molecular elevation for 100 grams, 26.5°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	83.00	0.2077	0.2502	0.022°	731.7	301
2	"	0.4265	0.5139	0.044	731.6	310
3	"	0.6638	0.7998	0.057	731.4	372
4	"	0.9418	1.1347	0.084	731.2	358

Barometer 731.8 — 731.2 mm.

Molecular weight at infinite dilution 285.0

Molecular elevation at infinite dilution 26.8°

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
5	87.96	0.5624	0.6394	0.056°	751.3	303
6	"	1.1489	1.3062	0.116	751.3	298
7	"	1.7543	1.9944	0.175	751.3	302
8	"	2.3488	2.6703	0.230	751.3	308
9	"	3.0083	3.4201	0.296	751.2	306

Barometer 751.2 — 751.2 mm.

Molecular weight at infinite dilution 288.0

Molecular elevation at infinite dilution 26.5°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
10	83.66	0.4760	0.5690	0.054°	738.6	279
11	"	1.0070	1.2037	0.106	738.4	301
12	"	1.6022	1.9151	0.164	738.1	309
13	"	2.2003	2.6301	0.217	737.9	321

Barometer 738.7 — 737.9 mm.

Molecular weight at infinite dilution 289.0

Molecular elevation at infinite dilution 26.4°

IV.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
14	85.52	0.5797	0.6779	0.057°	728.9	315
15	"	1.2161	1.4220	0.120	728.8	314
16	"	1.8741	2.1914	0.179	728.6	324
17	"	2.5856	3.0234	0.239	728.3	335

Barometer 728.9 — 728.3 mm.

Molecular weight at infinite dilution	295.0
Molecular elevation at infinite dilution	25.9°

V.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
18	86.80	0.4676	0.5387	0.051°	738.9	280
19	"	1.5308	1.7636	0.173	739.1	270
20	"	2.0444	2.3553	0.221	739.1	282
21	"	2.6930	3.1025	0.300	739.2	274

Barometer 739.8 — 739.2 mm.

Molecular weight at infinite dilution	281.0
Molecular elevation at infinte dilutiion	27.2°
Average of molecular weights at infinite dilution	287.6

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Benzene by the Boiling-Point Method.

(See diagram on opposite page.)

These results, it will be seen, point to S_8 as the molecular formula for sulphur and confirm those obtained by us, using toluene and carbon disulphide as solvents.

Results with Naphthalene.—As it is almost certain from the vapor density determinations of sulphur, which have been recorded, that the molecular weight of this substance at temperatures slightly above its boiling-point (448°C) is, at any rate, not greater than 256, it seemed to us probable that in liquids of high boiling-point the molecular weight would be less than 288, and possibly would be 256. We therefore selected naphthalene for the next solvent for this work. Notwithstanding its great tendency to sublime, it is an excellent solvent for molecular weight determinations by the boiling-point method. It is very easily obtained pure, and as sulphur is very soluble in it, the results are quite satisfactory.

The following table gives the results obtained :

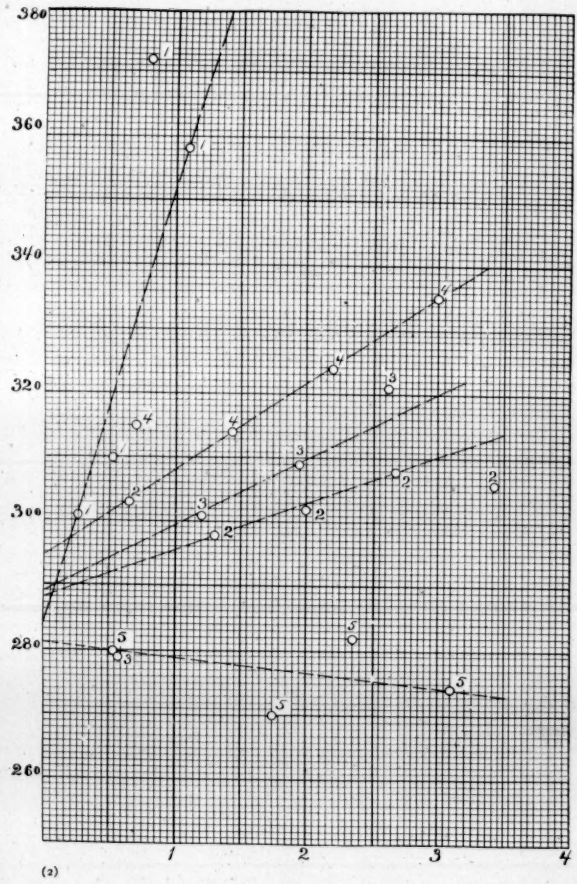
SULPHUR,

$S_8 = 256$; $S_9 = 288$.

Solvent : *Naphthalene.*

Boiling-point 216.7° C. at 741.9 mm. barometric pressure.

Molecular elevation for 100 grams 60.7°.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I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	89.75	0.4146	0.4619	0.104°	736.1	270
2	"	0.8194	0.9130	0.210	736.2	264
3	"	1.1788	1.3134	0.294	736.3	271
4	"	1.6380	1.8251	0.416	736.3	266
5	"	2.2252	2.4793	0.552	736.3	273
6	"	2.7823	3.1000	0.700	736.3	269
7	"	3.4758	3.8728	0.861	736.4	273
8	"	4.1324	4.6043	1.013	736.4	273

Barometer 736.1 — 736.4 mm.

Molecular weight at infinite dilution 262.0

Molecular elevation at infinite dilution 59.5°

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
9	104.92	0.6123	0.5836	0.137°	745.8	259
10	"	1.2037	1.1473	0.270	"	258
11	"	1.7581	1.6757	0.398	"	256
12	"	2.3158	2.2072	0.525	"	255
13	"	2.8983	2.7624	0.662	"	253
14	"	3.4694	3.3067	0.785	"	256
15	"	4.0452	3.8555	0.897	"	261
16	"	4.6793	4.4599	1.022	"	265

Barometer 745.8 mm.

Molecular weight at infinite dilution 252.0

Molecular elevation at infinite dilution 61.7°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
17	101.72	0.4298	0.4225	0.096°	748.4	267
18	"	0.9585	0.9423	0.218	748.3	262
19	"	1.4654	1.4406	0.332	748.3	263
20	"	2.0161	1.9820	0.455	748.3	264
21	"	2.5409	2.4979	0.565	748.3	268
22	"	3.0615	3.0097	0.679	748.2	269
23	"	3.5759	3.5154	0.785	748.2	272
24	"	4.1437	4.0736	0.905	748.2	273

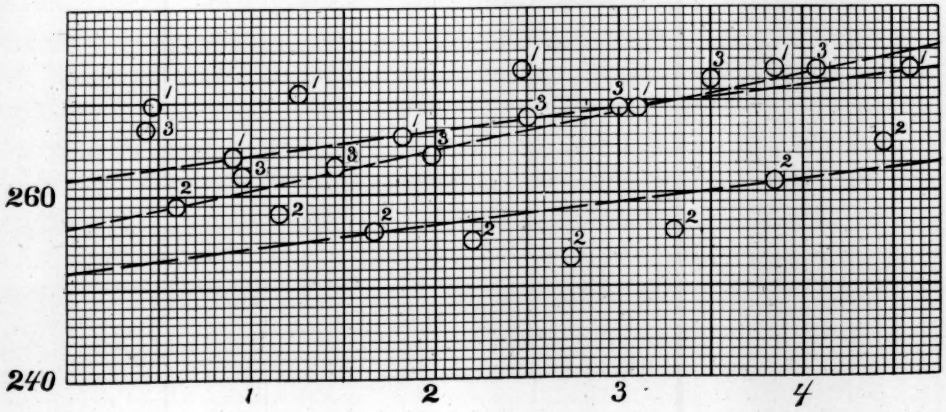
Barometer 748.4 — 748.2 mm.

Molecular weight at infinite dilution 256.5

Molecular elevation at infinite dilution 60.5°

Average of molecular weights at infinite dilution 256.8

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Naphthalene by the Boiling-Point Method.



These results can be interpreted in only one way, namely, that at the boiling-point of naphthalene the molecular weight of sulphur is 256 and that there are eight atoms in the molecule of sulphur at this temperature.

Results with Metaxylene. — Having thus shown that the molecular weight of sulphur is a function of the temperature we wished next to see if this change continued with the increase of temperature, but though we tried a large number of solvents[1] boiling over 200° C. we found none which would dissolve sulphur without decomposition. At this temperature sulphur appears indeed to be very active chemically. Certain solvents were found, however, whose boiling-points lie between those of toluene and naphthalene upon which sulphur did not act. Determinations were therefore made with these substances in order to find out what the molecular weight of sulphur was at temperatures between 100° and 200° C. The following are the results with metaxylene:

SULPHUR,

$S_8 = 256$; $S_8 = 288$.

Solvent: *Metaxylene.*

Boiling-point 138.8° C. at 756.1 mm. barometric pressure.

Molecular elevation for 100 grams, 43.2°.

I.

	Grams solvent.	Grams substance	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	77.13	0.8067	1.0459	0.180°	748.8	251
2	"	1.5990	2.0731	0.333	748.8	269
3	"	2.3771	3.0819	0.475	749.0	280
4	"	3.1933	4.1401	0.626	749.0	286
5	"	3.8914	5.0452	0.750	749.0	291
6	"	4.6038	5.9689	0.868	749.0	297
7	"	5.1124	6.6283	0.950	749.1	301

Barometer 748.8 — 749.1 mm.

Molecular weight at infinite dilution 250.0

Molecular elevation at infinite dilution 44.2°

[1] Sulphur is but slightly soluble in or acts upon the following substances at their boiling-points: fluorene, phenanthrene, diphenylmethane, ethylene bromide, ethyl acetate, mesitylene, resorcin, diphenyl, quinoline, monobromnaphthalene, acenaphthene, dihydroanthracene, diphenylketone, acetanilide, phthalic anhydride, anthracene, amyl benzoate, ether, alcohol, acetic acid, heptane and chloroform.

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
8	72.37	0.3889	0.5374	0.092°	746.2	252
9	"	0.8102	1.1195	0.175	746.2	276
10	"	1.2724	1.7582	0.263	746.3	289
11	"	1.6885	2.3331	0.342	746.3	295
12	"	2.1421	2.9599	0.432	746.4	296
13	"	2.6924	3.7203	0.544	746.4	295
14	"	3.2286	4.4612	0.651	746.4	296
15	"	3.7982	5.2484	0.763	746.5	297

Barometer 746.2 — 746.5 mm.

Molecular weight at infinite dilution 255.0

Molecular elevation at infinite dilution 43.4°

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
16	68.25	0.5163	0.7565	0.119°	747.0	275
17	"	1.0547	1.5453	0.224	746.9	298
18	"	1.5951	2.3371	0.329	746.9	307
19	"	2.1668	3.1748	0.441	746.8	311
20	"	2.6787	3.9248	0.538	746.8	315
21	"	3.1584	4.6277	0.632	746.8	316
22	"	3.6649	5.3698	0.734	746.7	316
23	"	4.1460	6.0747	0.834	746.7	314

Barometer 747 — 746.7 mm.

Molecular weight at infinite dilution 261.0

Molecular elevation at infinite dilution 42.4°

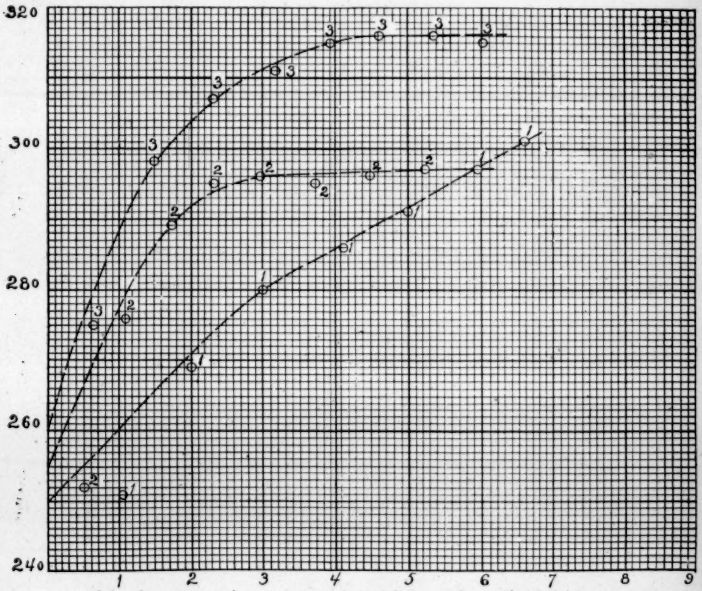
Average of molecular weights at infinite dilution 255.3

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Metaxylene by the Boiling-Point Method.

(For diagram see next page.)

Notwithstanding the rapid increase of the molecular weight with increasing concentration these results show that even at the boiling-point of metaxylene the molecular weight of sulphur is 256 and that the change from S_8 to S_6 takes place somewhere between 110° C. and 140° C.

Results with Phenetol.—In all the work previously done,



with the exception of that in which carbon disulphide was used, the solvents have been hydrocarbons. It seemed highly desirable that these results should be confirmed, if possible, with solvents of a different character. For this purpose we selected anisol, phenetol, and phenol, which are excellent solvents for sulphur and for molecular weight determinations. Unfortunately the work with anisol was not completed owing to an accident involving the loss of all the material we had on hand. The following are the results with phenetol:

SULPHUR,

$S_s = 256$; $S_o = 288$.

Solvent: *Phenetol.*

Boiling-point 168.3° C. at 756.1 mm. barometric pressure.

Molecular elevation for 100 grams, 49.3°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	117.60	1.0005	0.8508	0.159°	744.4	264
2	"	1.8669	1.5875	0.280	744.4	280
3	"	2.7589	2.3460	0.402	744.3	288
4	"	3.6110	3.0706	0.520	744.3	291
5	"	4.4206	3.7590	0.633	744.2	293
6	"	5.3169	4.5212	0.750	744.2	297
7	"	6.1444	5.2248	0.853	744.2	302
8	"	6.8472	5.8224	0.943	744.1	304

Barometer 744.4 — 744.1 mm.

Molecular weight at infinite dilution **257.0**

Molecular elevation at infinite dilution **49.1°**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
9	113.88	0.8177	0.7180	0.136°	742.5	260
10	"	1.6025	1.4072	0.259	742.6	268
11	"	2.2771	1.9996	0.363	742.6	272
12	"	3.0257	2.6569	0.470	742.6	279
13	"	3.7132	3.2606	0.570	742.6	282
14	"	4.4323	3.8921	0.675	742.6	284
15	"	5.1957	4.5624	0.782	742.6	288
16	"	5.8743	5.1583	0.875	742.7	291

Barometer 742.5 — 742.7 mm.

Molecular weight at infinite dilution **255.0**

Molecular elevation at infinite dilution **49.5°**

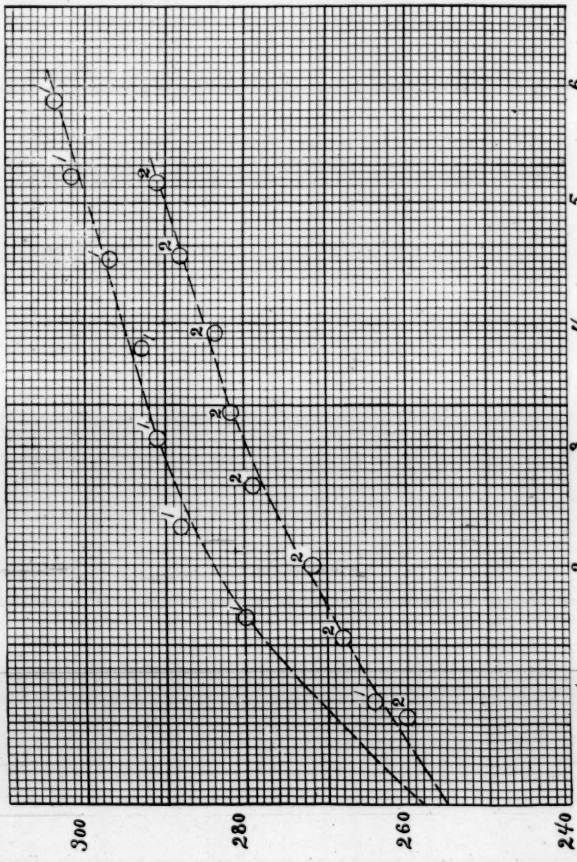
Average of molecular weights at infinite dilution **256.0**

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Phenetol by the Boiling-Point Method.

(For diagram see next page.)

It is obvious from these results that the molecular weight of sulphur at the boiling-point of phenetol is 256.

Results with Phenol.—The next solvent employed was phenol and although a slight trace of sulphuretted hydrogen is evolved on long continued boiling this solvent with sulphur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the action is so slight that it does not seem to interfere with molecular weight determinations in this liquid. Sulphur is very soluble in phenol at its boiling-point and this solvent is an excellent one for this work on account of the ease with which it is obtained pure and because the molecular weight of sulphur only increases slightly with increase of concentration. Of course the solvent must be protected from moisture by using a tube filled with calcium chloride. The following table gives the results with this solvent:

SULPHUR,

$S_6 = 256$; $S_8 = 288$.

Solvent: *Phenol.*

Boiling-point 181° C. at 755.9 mm. barometric pressure.

Molecular elevation for 100 grams, 30.4°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	114.05	1.3706	1.2018	0.145°	740.9	252
2	"	2.6329	2.3086	0.278	740.9	252
3	"	4.1131	3.6064	0.429	741.0	256
4	"	5.4603	4.7876	0.569	741.0	256
5	"	6.3172	5.5390	0.660	741.0	255
6	"	7.2016	6.3144	0.744	741.2	258
7	"	7.7975	6.8369	0.806	741.3	258

Barometer 740.9 — 741.3 mm. Average of series I 255.3

Moleculer weight at infinite dilution 251.0

Molecular elevation at infinite dilution 31.0°

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
8	116.92	1.7948	1.5351	0.185°	744.2	252
9	"	3.3002	2.8226	0.335	744.2	256
10	"	4.7407	4.0547	0.488	744.2	253
11	"	6.3211	5.4063	0.627	744.2	262
12	"	7.9668	6.8139	0.776	744.2	267
13	"	9.6218	8.2294	0.920	744.1	272
14	"	10.4795	8.9630	0.990	744.1	274
15	"	11.3667	9.7218	1.078	744.1	274

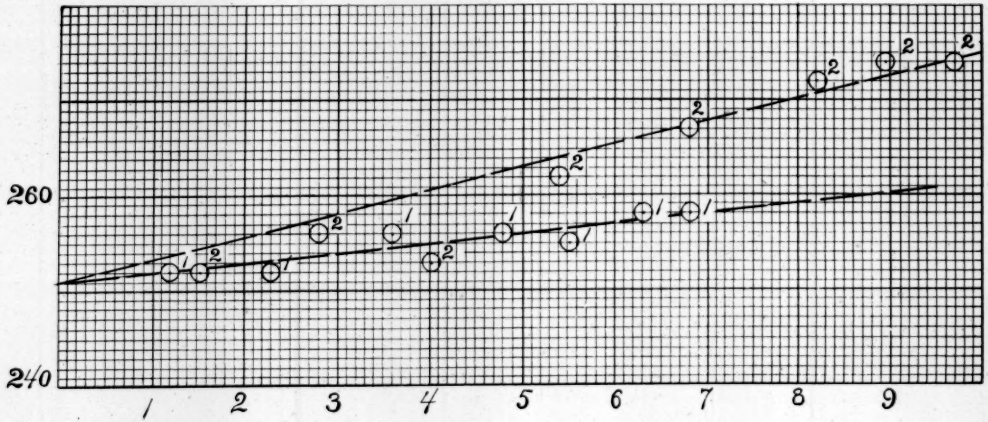
Barometer 744.2 — 744.1 mm. Average of series II. 263.7

Molecular weight at infinite dilution 251.0

Molecular elevation at infinite dilution 31.0°

Average of 15 determinations in phenol 259.5

Graphic Representation of Determinations of Molecular Weight of Sulphur in Phenol by the Boiling-Point Method.



These results confirm in a most striking manner those obtained with metaxylene and phenetol and leave no doubt as to the molecular weight of sulphur at the temperature of boiling phenol.

Results with Sulphur Chloride, (S_2Cl_2).—We have purposely left the recording of the results obtained by the boiling-point method with this solvent till last because of their surprising character and because of the difficulties experienced in working with this liquid. The substance not only has an extremely disagreeable odor and attacks the mucous membrane of the eyes and nose, but it also deposits sulphur wherever it comes into contact with moisture and decomposes rubber and cork with amazing rapidity. Although it is such an unpleasant liquid to work with, it is a most excellent solvent for sulphur. We purified the material by distilling it from sulphur and fractioning until it had a constant boiling-point.

As no reliable data exist as to the heat of vaporization of this substance we calculated the molecular elevation for 100 grams from the boiling-point given by Thorpe (138.12° C. at 760 mm.). This constant[1] was then shown to be very nearly correct by determining the molecular weight of triphenylmethane in sulphur chloride. Owing to the solvent action of sulphur chloride on rubber and cork it was impossible to make a long series with this liquid. The products of the action of the liquid on the stopper go into solution, causing the boiling-point to gradually rise. To overcome this difficulty we made short series working as quickly as possible or made individual determinations, introducing comparatively large quantities of substance to get large rises of temperature. This was easy to do as the material dissolved very readily and readings could be obtained within two minutes after introducing it. We give first the results with triphenylmethane to show that the method is reliable and then those with sulphur.

TRIPHENYLMETHANE,

$CH(C_6H_5)_3 = 244$.

Solvent: *Sulphur Chloride*, (S_2Cl_2).

Boiling-point 136.6° C. at 745.7 mm. barometric pressure.

Molecular elevation for 100 grams, 52.8°.

$$^1K = \frac{0.0198 \times 411.12 \times 135}{20.81} = 52.8.$$

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	204.49	1.5430	0.7546	0.168°	739.3	237
2	"	2.6777	1.3094	0.298	739.3	232
3	204.49	1.5912	0.7781	0.169	739.6	243
4	"	3.2081	1.5688	0.349	739.6	237
5	"	4.4116	2.1574	0.499	739.6	228
6	204.49	1.1803	0.5772	0.127	739.6	240
	Average of determinations					236.0

SULPHUR,

$S_2 = 64$; $S_3 = 96$.

Solvent: *Sulphur Chloride*, (S_2Cl_2).

Boiling-point 136.6° at 745.7 mm. barometric pressure.

Molecular elevation for 100 grams, 52.8°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
1	210.18	0.4725	0.2248	0.200°	745.3	59
2	"	1.0743	0.5111	0.475	745.2	57
	Average of series I					58.0

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
3	214.05	0.9490	0.4433	0.455°	748.1	51
4	"	0.8872	0.4145	0.340	748.1	64
5	"	0.9097	0.4250	0.345	748.1	65
6	"	0.8499	0.3971	0.290	748.0	72
7	"	0.7151	0.3341	0.251	748.0	70
	Average of results					64.4

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
8	219.64	1.0688	0.4866	0.504°	742.4	51
9	"	0.9095	0.4141	0.377	742.4	58
10	"	0.9987	0.4547	0.369	742.3	65
11	"	0.8433	0.3839	0.283	742.3	72
12	"	0.8692	0.3957	0.294	742.2	71
	Average of results					63.4

Average of 12 determinations in sulphur chloride 61.9

If these results be plotted in the regular way with the molecular weights as ordinates and the concentrations as abscissas they give for the molecular weight of sulphur at infinite dilution values very near 64.

We then made determinations in this solvent at greater concentrations. As the molecular weight increases quite rapidly with the increase in concentration the molecular weight at infinite dilution must be taken here as the true value. The following are the results obtained in this way.

SULPHUR,

$S_2 = 64$.

13.3588 grams sulphur introduced at first for concentration effect.

Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed elevation.	Barometer mm.	Molecular weight.
210.37	1.1652	0.5539	0.225°	747.8	130
"	1.1032	0.5244	0.202	747.8	137
"	0.9332	0.4436	0.162	747.9	145
"	0.9100	0.4326	0.155	747.9	147
Molecular weight at infinite dilution					55.0

These results indicate that the molecular weight of sulphur in sulphur chloride is 64 and the molecular formula is S_2. In this solvent, therefore, a dissociation of the sulphur molecules S_8 and S_6 takes place entirely analogous to that observed when sulphur is heated to a comparatively high temperature (860°–1700° C.).

Determinations of the Molecular Weight of Sulphur by the Freezing-Point Method.

Results with Naphthalene.—Having obtained the above results with the boiling-point method it was thought important to see if like values for the molecular weight of sulphur could be found by the freezing-point method also. We therefore first repeated the work of Hertz[1] using naphthalene as a solvent. This substance is an excellent solvent for sulphur and there is no difficulty in obtaining good readings with it. We made use of the ordinary Beckmann apparatus and the same thermometer used in the previous work but instead of striking the thermometer occasionally, as usually recom-

[1] This comprised a series of only *three* determinations.

mended, we arranged an electric hammer so that it struck the metal top of the thermometer continuously, while the determination of the freezing-point of the solvent was being observed. The following are the results obtained:

SULPHUR,

$S_7 = 224$; $S_8 = 256$.

Solvent: *Naphthalene.*

Freezing-point 79.4° C. at 752 mm. barometric pressure.

Boiling-point 217.5° C. at 743.5 mm. barometric pressure.

Molecular depression for 100 grams, 69.4°.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
1	27.624	0.2741	0.9923	0.296°	233
2	"	0.5221	1.8900	0.530	247

Molecular weight at infinite dilution **219.0**

II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
3	28.349	0.2864	1.0103	0.299°	234
4	"	0.6600	2.3281	0.665	243
5	"	0.8330	2.9384	0.823	248
6	"	1.0572	3.7293	1.015	255
7	"	1.3351	4.7095	1.245	262
8	"	1.7351	6.1205	1.593	267

Molecular weight at infinite dilution **226.0**

III.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
9	31.539	0.3764	1.1934	0.340	244
10	"	0.7566	2.3989	0.664	251

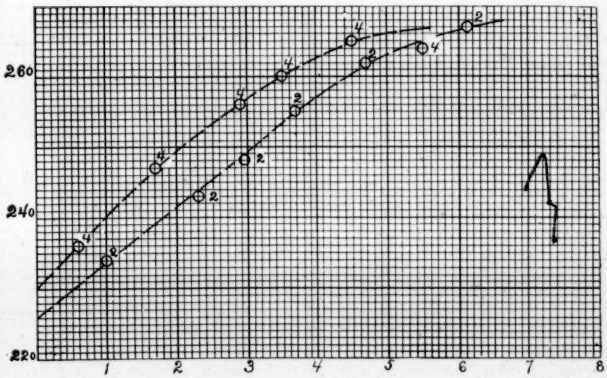
Molecular weight at infinite dilution **237.0**

IV.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
11	29.235	0.1771	0.6058	0.178°	236
12	"	0.4976	1.7021	0.478	247
13	"	0.8459	2.8934	0.783	256
14	"	1.0299	3.5228	0.940	260
15	"	1.3228	4.5247	1.183	265
16	"	1.6075	5.4985	1.446	264

Molecular weight at infinite dilution	230.0
Average of molecular weights at infinite dilution	228.0

Graphic Representation of Determinations of the Molecular Weight of Sulphur in Naphthalene by the Freezing-Point Method.



These results, indicating that the molecular weight of sulphur at the freezing-point of naphthalene is 224, were so surprising and so different from Hertz's results and from those in benzene, at the same temperature, by the boiling-point method, that we at first thought some error had been made. But a repetition of the work only demonstrated its correctness. That the molecular weight of sulphur should be 256 at the boiling-point of naphthalene and 224 at the freezing-point of the same solvent is utterly inconceivable. There must be some error in the freezing-point method of determining molecular weights in the case of this substance. Possibly it may be that the determinations are made too near the cryohydrate temperature of sulphur and naphthalene (74°C), which is only five degrees below the freezing-point of naphthalene. Other examples of abnormal values for the molecular weights by the

freezing-point method are well known, though so far as we are aware no good explanation[1] of these anomalies has been given. The explanation offered by Beckmann and Stock[2] for the peculiar results obtained by them for the molecular weight of iodine in benzene solution, *viz.*, that the solid which separates out when the temperature of the solvent is lowered to determine its freezing-point contains iodine will not apply here as the material solidifying was shown to be only naphthalene by examination with the microscope.

Results with Diphenyl.—We endeavored next to find a solvent[3] for sulphur whose freezing-point was not so near the cryohydrate temperature, but without success. Sulphur is either too slightly soluble in solvents that solidify at temperatures that can easily be obtained or else it acts on them at their melting-point or the freezing-point and cryohydrate points lie very close together. We found that diphenyl was an excellent solvent for sulphur, however, and though the cryohydrate temperature of this solvent with sulphur (64.7° C.) is very near its freezing-point, 68.2° C., still we made molecular weight determinations with this substance by the freezing-point method to see if they would confirm the abnormal values obtained with naphthalene. The method and apparatus were the same as those used with naphthalene. The following table gives the results :

SULPHUR,

$S_7 = 224$; $S_8 = 256$.

Solvent : *Diphenyl.*
Freezing-point 68.2° C. at 752 mm. barometric pressure.
Boiling-point 255.3° C. at 743.6 mm. barometric pressure.
Molecular depression for 100 grams, 82.6°.

[1] Van't Hoff's explanation (Ztschr. phys. Chem., **5**, 334) that a solid solution of the solvent with the dissolved substance separates out instead of the pure solvent when the temperature is lowered to the freezing-point only holds for some of the cases. See in this connection the results of Auwers using benzene and naphthalene as solvents (Ztschr. phys. Chem., **12**, 689, and Ber. d. chem. Ges., **28**, 2878).

[2] Ztschr. phys. Chem., **17**, 120.

[3] The following are some of the solvents we tried : thymol, phenol, benzene, acetic acid, diphenylmethane, anethol, nitrobenzene, aethal and ethylene bromide.

I.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
1	22.939	0.4546	1.9818	0.626°	261
2	"	0.8044	3.5067	1.070	271
3	"	1.1873	5.1759	1.528	280
4	"	1.5471	6.7444	1.932	288

Molecular weight at infinite dilution 252.5

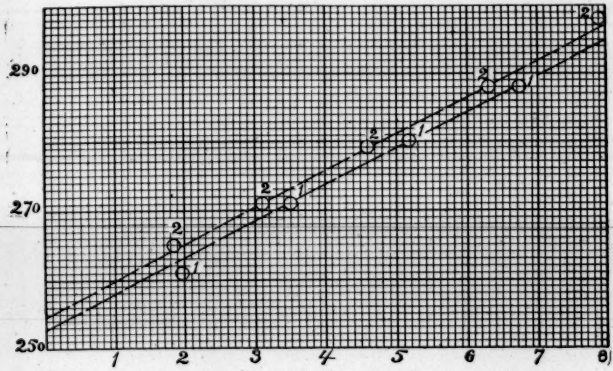
II.

	Grams solvent.	Grams substance.	Concentration in 100 grams.	Observed depression.	Molecular weight.
5	21.073	0.3839	1.8218	0.568	265
6	"	0.6581	3.1230	0.951	271
7	"	0.9693	4.5997	1.360	279
8	"	1.3238	6.2820	1.800	288
9	"	1.6644	7.8983	2.193	298

Molecular weight at infinite dilution 254.5

Average of molecular weights at infinite dilution 253.5

Graphic Representation of Molecular Weight Determinations of Sulphur in Diphenyl by the Freezing-Point Method.



These results indicate that the molecular weight of sulphur in diphenyl at the freezing-point of this solvent is 256 and not 224, the value found using naphthalene as a solvent.

We are not inclined to give much weight, however, to either of the values found for the molecular weight of sulphur by the freezing-point method, first, because they do not agree with each other, and secondly, because neither agrees with the single value (288), found by the boiling-point method in carbon disulphide, benzene, and toluene. Probably the same explanation will be found to hold for these peculiar results in naphthalene and diphenyl. It is certainly significant that in both cases the cryohydrate temperature lies so close to the freezing-point of the solvent. We have given these results here simply to call the attention of chemists to them and in the hope that some explanation may be ultimately offered of their anomalous character.

Summary.

The results of this investigation on the molecular weight of sulphur may be briefly summarized as follows:

1. The molecular weight of sulphur in carbon disulphide, benzene, and toluene is 288 and we must conclude, therefore, that, at the boiling-points of these liquids, the molecular formula of sulphur is S_8. These temperatures, it will be noted, are all below the melting-point of sulphur.

2. In metaxylene, phenetol, phenol, and naphthalene, on the other hand, the molecular weight of sulphur is 256, and hence the molecular formula is S_8 at the temperatures represented by the boiling-points of these solvents, *i. e.*, at temperatures above the melting-point of sulphur.

3. In sulphur chloride the molecular weight of sulphur is 64 and the molecular formula must therefore be S_2. Complete dissociation of the more complex sulphur molecules takes place in this solvent, the results being in close agreement with those obtained by the vapor density method at high temperatures (860–1700° C.).

4. Determinations of the molecular weight of sulphur in naphthalene and diphenyl by the freezing-point method cannot be relied upon in deciding the question of the molecular weight of this element, since the results obtained do not agree with each other nor with those obtained at the same temperatures by the boiling-point method. In naphthalene 224 was

the value found, pointing to a molecule S_7, while in diphenyl 256, indicating a molecule S_8 resulted.

5. The molecular weight of both the orthorhombic and the monoclinic varieties of sulphur is the same (288), since from boiling carbon bisulphide only orthorhombic sulphur crystallizes out while from boiling benzene and toluene monoclinic sulphur alone separates, and since the molecular weight of sulphur in all these solvents is the same, 288.

CORNELL UNIVERSITY, ITHACA, N. Y.,
January, 1896.

Contributions from the Chemical Laboratory of Case School of Applied Science.

XXII.—ON THE DETERMINATION OF SULPHUR IN ILLUMINATING GAS AND IN COAL.

BY CHARLES F. MABERY.

Having recently been called upon to make some determinations of sulphur in illuminating gas, in considering the various methods for this determination I was impressed with the need of an accurate method, which should be at the same time capable of giving desirable results without too close attention. So far as I am aware, all the methods in use depend upon the combustion of a definite volume of gas and passing the products through bromine water or a similar reagent for oxidation and absorption. The sulphuric acid formed is precipitated as baric sulphate. Such methods require an atmosphere free from sulphur in any form, which it is sometimes difficult to obtain in the laboratory. The volume of gas burned must be large to obtain a sufficient weight of baric sulphate, and precipitation in this form is always wasteful of time, whenever it can be replaced by more expeditious means of reaching the desired result. Then it is difficult to adjust lamps to burn regularly without considerable attention.

When Sauer first proposed his method for the determination of sulphur in organic bodies, he suggested that it could be applied to the estimation of sulphur in gases, although he gave no data to demonstrate its efficiency. Valentine[1] had previously devised a method on somewhat the same principle, in which the gas to be burned was mixed with air before it entered the combustion tube. To ensure complete combus-

[1] Chem. News, 17, 89.

tion the gaseous mixture was carried over platinum sponge, and for absorption the products of combustion were carried through an oxidizing solution, such as potassic chlorate and hydrochloric acid. Valentine found it extremely difficult to completely oxidize and absorb the sulphur. Almost invariably, he states, traces of sulphurous acid were found in his last tower. He further says, "it was evident that no reliance could be placed on the oxidation and absorptive power of the various solutions. Gaseous sulphurous acid is not so readily oxidized nor retained when mixed with an overwhelming amount of other gases, as is generally supposed."

Knublauch[1] burned 15–20 liters in about an hour in an ignition tube containing platinized asbestos, and absorbed the sulphur in potassic carbonate. The amount of sulphur he obtained per cubic meter was between 0.3971 and 0.3135 gram. This wide variation was doubtless due, at least in part, to differences in the composition of the gas.

The first of several methods based on the combustion of gas in a lamp, was described by Letheby.[2] The gas was burned in a funnel-tube and the products carried forward into a wide horizontal tube, washed out, and the acid precipitated with baric chloride. Mixter[3] burned the gas from a platinum-tipped glass tube in a large glass flask (15 liters) in an atmosphere of oxygen, keeping the flask cold, and precipitating with baric chloride. Poleck[4] used a Bunsen lamp to burn the gas, within a wide glass tube, and led the products forward into a solution of sodic hydrate and bromine.

The apparatus of Drehschmidt,[5] constructed on the same principle and now recommended, consists of a special form of lamp for burning the gas within an upright tube closed at the base except for the introduction of air. The necessity of an atmosphere free from sulphur is evident. Fairley[6] suggested the use of hydrogen dioxide as an oxidizing agent.

From the general applicability to the determination of sulphur in oils, asphalts, and other organic bodies, of the method described by me,[7] it seemed possible to apply this method

[1] Ztschr. anal. Chem., **21**, 335.
[2] Chem. News, **7**, 73.
[3] This JOURNAL, **2**, 244.
[4] Ztschr. anal. Chem., **22**, 171.
[5] Ztschr. anal. Chem., **29**, 625.
[6] Ztschr. anal. Chem., **29**, 628.
[7] This JOURNAL, **16**, 544.

with suitable modifications to the determination of sulphur in gases.

As in the analysis of oils with minute quantities of sulphur, I found it advantageous to absorb the products of combustion in a centinormal solution of sodic hydrate. Even in such a dilute alkaline solution and with the rapid current of air necessary to maintain the combustion, the sulphuric acid formed is retained with remarkable persistence. As stated in the publication of my results with oils, it was assumed that a considerable excess of the absorbing solution was necessary to avoid loss, on account of the great dilution of the minute quantity of sulphuric acid by the large excess of air. To be sure that no sulphur was lost in the combustion of gas by incomplete absorption, a second absorption tube containing the centinormal alkaline solution was attached in front. Upon titration no change in the standard of the alkaline solution in the second tube could be detected. In this experiment a larger volume of gas was accidentally burned than was intended, and upon titration it was found that the alkaline solution in the first absorption tube had been almost entirely neutralized; there remained only 2 cc. of free alkali. There is, therefore, not the slightest danger of loss from incomplete absorption.

The form of apparatus best adapted for the determination of sulphur in gases by this method is shown in the accompanying figure. The U tube should be of considerable size.

In the analyses described in this paper, the tube used was 34 cm. in height and 25 mm. inside diameter. Above the bend for 8 cm. it is filled with broken glass, which subdivides the bubbles, and brings the gas into intimate contact with the absorption solution. The ignition tube should be 45.50 cm. in total length, and the constriction 30 cm. from the forward end. Air is drawn in from outside the laboratory and admitted

through a tube into the rear end of the combustion tube. A rapid current is necessary, and it may be maintained by means of a water pump or any other form of suction pump. For the introduction of the gas to be burned, a tube of hard glass about 2 mm. inside diameter is introduced far enough to deliver the gas just beyond the narrowest point of the constriction. A tube of this size will support a flame 3 cm. in length without depositing soot, which must be avoided. Depending on the size of the delivery tube, the gas may be burned in a continuous flame or in flashes. After setting the meter for measurement, and regulating the size of the flame, the operation needs no further attention until a sufficient quantity of gas has been burned. To regulate the flow of gas, it is convenient for better observation to introduce a wash-bottle with a very little water between the meter and the combustion tube, with a nipper-tap between the meter and wash-bottle.

Titration is made either in the ∪ tube or in a beaker with centinormal sulphuric acid with methyl orange as an indicator. The results of which this method is capable are shown by the following analyses, which were the first obtained in applying this form of combustion :

1. 5.6 liters of gas at 18°, bar. 750 mm., neutralized 6.5 cc. NaOH, equivalent to 0.001073 gram sulphur.

2. 5.6 liters of gas, at 18°.5, bar. 747 mm., neutralized 7.0 cc. NaOH, equivalent to 0.001155 gram sulphur.

3. 5.6 liters of gas, at 18°.5, bar. 747 mm, neutralized 6.8 cc. NaOH, equivalent to 0.001122 gram sulphur.

4. 11.2 liters of gas at 18°.5, bar. 747 mm., neutralized 13.8 cc. NaOH, equivalent to 0.002277 gram sulphur.

5. 28 liters of gas, at 17°, bar 746 mm,, neutralized 33 cc. NaOH, equivalent to 0.005445 gram sulphur.

	Sulphur found.	
	Grams per cubic meter.	Grains per cubic foot.
1	0.2027	0.089
2	0.2118	0.093
3	0.2186	0.096
4	0.2165	0.095
5	0.2095	0.092

While these results are not far outside the limits of error, the determinations were made on different days, and there is

doubtless slight variation in the sulphur remaining in the gas after the purification.

The statement of Valentine, given above, conveys the impression that under no circumstances can the sulphur in combustion be completely oxidized to sulphuric acid. If this were true, evidently no reliance could be placed on results of titration without oxidation, since, as is well-known, methyl orange is not sensitive to acid sodic sulphite. In general, our results with combustion have indicated that oxidation with oils and with gas is complete or very nearly so. Since hydrogen dioxide is the only convenient oxidizing agent that can be used in a solution that is to be titrated, it seemed worth while to ascertain beyond question whether, by means of this reagent, the oxidation is complete. A dilute solution of sulphurous acid was neutralized by a centinormal solution of sodic hydrate, and a few drops of an acid-free solution of hydrogen dioxide added. Immediately the solution became a deep pink, showing the formation of the acid sulphate by oxidation, and also that the oxidizing power of hydrogen dioxide could be depended on to convert any trace of sulphurous into sulphuric acid. A determination of sulphur in gas was then made, passing the gases from the combustion tube through two absorption tubes. Titration of the centinormal solution of sodic hydrate in the second tube showed no change. Hydrogen dioxide was then added and the solution again titrated. There was still no change, proving beyond question that all the sulphur was retained in the first absorption tube. After the latter solution was made neutral with decinormal acid, the addition of hydrogen dioxide produced no change. There can, therefore, be no doubt that in this form of combustion the oxidation is complete.

After a great number of sulphur determinations in asphalts, coal tar, and all varieties of petroleum products, and now in gas, we are convinced that this method leaves nothing to be desired in point of accuracy or simplicity for the analysis of any organic compounds which leave no inorganic residue.

For valuable aid in studying this method of analysis, I am indebted to my assistant, Mr. E. Davidson.

Determination of Sulphur and Ash in Coal.

Of the various methods for the determination of sulphur in coal depending on oxidation, none seems to be accurate and entirely satisfactory except the well-known method of Eschka proposed in 1874.[1] In point of accuracy this method seems to be capable of meeting the requirements of technical determinations, but the oxidation must not be carried on too rapidly, and it includes precipitation and manipulation of baric sulphate. In his first statement of the determination of sulphur by combustion, Sauer[2] suggested that his method might be applied to the analysis of coal, and Mixter also includes some analyses of coal in his modifications of the same method. This method, successfully applied, must evidently depend on a moderate rate of combustion, to ensure complete oxidation and absorption in the form of flasks employed, and the same objection to the manipulation of baric sulphate appears. If only a single determination is to be made, and that occasionally, it may be urged that this feature is of minor importance. But, in a long series of analyses, as in other operations when a volumetric method is capable of great accuracy, time may be saved by avoiding the gravimetric manipulations.

In a method depending on the oxidation and volatilization of the sulphur, the amount of sulphur remaining behind in the ash would be the determining feature. For if the ash must always be examined for the amount of sulphur retained, such a method would have no advantage over oxidation in a crucible. But, if no appreciable quantity, or an approximately constant quantity, remained in the ash, evidently the weight of the residue should afford a determination of the ash. It is to be expected that the proportion of sulphur retained should depend to a certain extent at least on the quantity of lime in the ash, with the question as to whether the lime retains its full equivalent of the sulphur. In most coals, lime is nearly or quite wanting, the sulphur being present as pyrite, which is frequently seen in coal heaps in large masses.

In general, the method we have followed is similar to the

[1] Ztschr. anal. Chem., **13**, 344. [2] Ztschr. anal Chem., **12**, 32.

estimation of sulphur in oils and asphalts. The coal is weighed in a platinum boat, which has been found to retain all the residue after oxidation. The combustion is carried on in a rapid stream of air entering at the constriction through the inner hard glass tube with a slower current entering through the rear tube to carry forward the volatile portion, and to assist the combustion. White fumes must not appear in the absorption tube. As in asphalts, some care is necessary in distilling the volatile portion, but in this respect coals require less attention than asphalts. Tubes of very hard glass are necessary to maintain a high temperature, although we have not ascertained how low a temperature is really essential. In all our work the temperature has been kept as high as the tube would stand. Under these conditions one combustion tube will serve, with ordinary care, for a great number of analyses. The length of the tube forward of the constriction need not be more than 40 cm., allowing for protection of the cork from burning, and the rear portion need not be more than 25 cm.

As shown in the figure we use a U tube of considerable size to allow the rapid stream of air to pass without danger of bubbles rising to the top of the tube. After some experience with details 0.5 gram of coal may be burned in a half hour, allowing twenty minutes for the distillation of volatile matter, and ten minutes for the combustion of fixed carbon. In burning cokes, the operation is more satisfactorily performed in oxygen. The absorbent solution used in these analyses was a tenth normal sodic hydrate. A little stronger solution, perhaps a fifth normal, would save some addition of the acid solution in titration. The final reaction is clearly defined, and the difference in colors between acid and alkaline is so clearly marked that the contrast is easily observed even in a hundredth normal solution. In the following table are given the results obtained in the analysis of a variety of coals :

	Weight taken.	cc. $\frac{n}{10}$ NaOH.	cc. $\frac{n}{10}$ H_2SO_4.	Per cent. sulphur.	Per cent. S_2 by the Eschka method.	Difference.	Weight of ash.	Per cent. of ash.	Per cent. of ash by old method.	Difference.	Per cent. S_2 in ash.	Lime.	Kind of coal.
1	0.5318	35.2	25.1	3.04	2.10	—0.12	0.0585	11.00	11.46	—0.46	0.10	absent	Bit. slack
2	0.4373	29.4	24.0	1.98		—0.07	0.0128	2.93	2.82	+0.11	0.05	"	"
3	0.4886	29.4	23.5	1.28	1.35	—0.07	0.0112	2.29	2.12	+0.17	0.07	present	Bit.
4	0.4900	35.2	32.7	0.80	0.76	+0.04	0.0094	1.91	1.79	+0.12	0.03	absent	"
5	0.4866	29.4	27.0	0.78	0.78	0.00	0.0076	1.58	1.44	+0.14	0.04	"	"
6	0.5086	35.2	28.2	2.21			0.0530	10.42	10.36	+0.06	0.04	"	"
	0.4956	29.4	22.4	2.23			0 0513	10.35		—0.01	0.04	"	"
7	0.5187	29.4	24.4	1.52	1.53	—0.01	0.0111	2.12	1.96	+0.16	0.06	"	"
8	0.5410	29.4	26.9	0.73	0.76	—0.03	0.0096	1.78	1.76	+0.02	0.02	"	Bit. slack
9	0.5280	29.4	26.7	0.82	0.89	—0.07	0.0092	1.74	1.69	+0.05	0.02	"	"
10	0.5161	35.2	20.5	4.55			0.0618	11.95			0.04	"	"
11	0.5003	29.4	22.4	2.21			0.0334	6.67			0.03	"	"
12	0.4949	35.2	31.5	1.21			0.0304	6.16			0.02	"	Anthracite
13	0.4843	29.4	27.6	0.58			0.0388	18.01			0.04	"	"
									Average S_2 in ash = 0.043				

The solutions used in titrations were not strictly decinormal, but were calculated on that basis that the volumes might be more readily comparable. 30 cc. of sodic hydrate, nearly decinormal, were actually taken for each absorption. It would have been interesting to have procured for analysis a variety of coals from representative districts, and to have established a mean of allowance for the sulphur remaining in the ash, but I was prevented from including this valuable information by great pressure of other affairs. The coals selected, however, present an average which, I think, may be accepted in general analysis for all coals with an ash not highly calcareous. This average, 0.043 per cent., probably represents as an outside limit the sulphur remaining in the ash. The close agreement in the percentages of ash found with other determinations, indicates a high degree of accuracy.

Reference to the column headed lime, shows that only in one instance was lime found in the ash, and here the quantity was not far from 0.05 per cent. With suitable modifications of this method, in an inert gas it would probably be possible to distil the volatile portion of the coal and weigh the residue of fixed carbon before completing the combustion for sulphur. But for want of time, I have not been able to put this suggestion to experimental proof.

For valuable aid in the analyses of these coals, I am indebted to Mr. R. A. Worstall, a student in this laboratory.

XXIII.—INVESTIGATIONS ON AMERICAN PETROLEUM.[1]

By Charles F. Mabery.

CHEMISTRY OF THE BEREA GRIT PETROLEUM.[2]

By Charles F. Mabery and Orton C. Dunn.

The deposits of petroleum in the Berea Grit and allied sandstones in Southern Ohio were among the first in the United States from which commercial products were prepared, yet nothing whatever is known concerning their composition

[1] For valuable aid in the prosecution of this work I desire to express my obligation to my assistants, Messrs. C. A. Soch and E. Davidson. I am also indebted for pecuniary aid to the C. M. Warren fund of the American Academy of Arts and Sciences.

[2] A portion of this work was presented by Mr. Dunn in a thesis for the Degree of Bachelor of Science.

except the very general knowledge necessary in processes of refining. In the geological column in this section four sandstones furnish oil, some of which have proved to be a prolific source since the early discovery of petroleum. Of these sources, the most important is the Berea Grit, which is below all the other sandstones. This formation, at least from a commercial point of view, is perhaps the most important in the Ohio geological scale; its outcrops supply a valuable building stone, and its submerged strata contain immense quantities of oil and gas, portions of which are collected under the requisite conditions to furnish a profitable supply. It extends over an area of more than 15,000 square miles in Ohio, and it continues into the adjoining states of Pennsylvania, New York, West Virginia and Kentucky. This geological formation was first investigated by Professor Newberry, who named it from the town in which it is best observed, where it furnishes large quantities of stone for construction. Since the discovery of oil, in connection with the drilling of wells, excellent opportunities for studying these strata as a reservoir of oil and gas were offered, and in connection with the labors of the state geological survey, under the direction of Professor Orton, much valuable information has been accumulated. This sandstone varies in thickness from a few feet to one hundred feet or more. For the most part it is a clean white material, quite variable as to coarseness from pebbles of considerable size to very fine sand. Except a few fossils and leaf impressions, the absence of organic remains is noteworthy. There is abundant evidence that it never was a source of petroleum, but it serves rather as a reservoir of oil that was forced up from the black shales beneath, in which the oil was originally formed. The impervious cover of the Berea Grit that holds in confinement the oil and gas is the Berea black shale, ten to fifty feet in thickness. Next above come the Cuyahoga shales, and the lower coal measures that contain at least four sandstones, each roofed with shales, and all these sandstones have yielded oil. With the hard shale overlying, and a soft floor, the Berea Grit is well adapted for the storage of oil. The composition of the Berea Grit sandstone is shown by the following results of our analyses:

	White oil sand.	Blue caprock.
Silica	92.30	91.80
Alumina	4.80	4.60
Ferric oxide	0.92	1.50
Calcium and magnesium oxides	0.28	0.34
Water combined	1.40	1.80
Total	99.70	100.04

In much of its extent the Berea Grit is too fine grained, and the strata too thin to allow of its carrying oil; but in a thickness of ten to fifty feet, and with the coarseness that exists in the oil sections, this sandstone carries one cubic foot of oil in every ten to twelve cubic feet of rock. Altogether during the present year the yield of oil from this source is 3,500 barrels daily or one twentieth of the yield from the Pennsylvania fields. In their best days the Macksburg and Eureka fields furnished one-tenth of the total supply; these fields are again on the increase from the gains in the Corning, Steubenville, and New Castle fields. The first oil obtained in this section in 1860, was well adapted for lubrication; it sold for $28.00 a barrel. The first important well, the "Elm Tree" well, started at 100 barrels in 1861. In 1864 $7,000,000 had been invested in oil companies in Washington and Noble counties alone. Oil in paying quantities was taken from the 140, 300, 500 and 700 foot sands. Since 1881 the Macksburg field has produced nearly 5,000,000 barrels of oil, but only one-third has come from the Berea Grit. All attempts to extend the Macksburg field have been unsuccessful. Oil is now obtained here only from shallow wells, chiefly from the 500 foot sand.

The Eureka field was first opened in 1886, and it is now equal in importance to the Macksburg field and more promising for the future. It lies near the Ohio river, extending four miles into West Virginia and three miles into Ohio. At one time 350 producing wells here yielded 4,500 barrels of oil daily, nearly all from the Berea Grit. At present the yield is about 1,000 barrels daily. The Berea Grit is here about 700 feet below sea level, and 1,350 feet below the level of the Ohio valley. It is between fifteen and thirty feet thick beneath a very black shale, which serves as a cover, approximately thirty feet thick. At first the rock pressure was very

great, but now the oil must be pumped. This field is connected with the Macksburg and Pennsylvania fields by a pipe line. The oil has a clear, amber color, with a beautiful fluorescence; it is very clean, and deposits little sediment even on long standing. The specimen of this oil used in our examination was from a well at Archer's Fork, Washington county, not far from the Ohio river. Oil was first obtained in the shallow wells at Mecca in 1861, in a territory which never exceeded in productive area more than a few hundred acres. The flow, never large, is now about 1,500 barrels annually of a good lubricating oil. Other fields, more or less promising, in which the Berea Grit yields oil, and in several sections gas in considerable quantities, include the Corning, New Castle, White Oak, West Virginia, Steubenville, and Cadiz territory. The Belden field, first opened in 1861, is now exhausted.

In undertaking an examination of the petroleum from this section, we procured specimens of the light amber oil from the Berea Grit, and from the principal sandstones of the lower coal measures which overlie this sandstone—the 140, 300, 500 and 700 foot strata—all of which are well developed in the Macksburg field. Petroleum from the 140 foot sand was procured from well No. 9, a small producer, on the Mosely farm, two miles north of Macksburg, where the sandstone is 158 feet deep and 14 feet thick. The composition and properties of the crude oil, which was of a light amber color, as well as the percentages and specific gravity of the distillates are given in the following table:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-Absorp.	HBr set free.
	85.00	13.77	0.027		0.8118	7.62	3.00
110°				0.55		0.74	0.20
110–135°				6.54		1.76	0.65
135–160°				8.38	0.7480	2.41	1.61
160–185°				6.00		2.24	1.36
185–210°				9.60	0.7760	2.32	0.94
210–235°				8.00		2.08	0.51
235–260°				6.60		3.87	0.52
260–285°				9.01		4.62	1.12
285–310°				6.60		5.69	1.93
310–335°				2.62		4.58	2.01
335–360°				11.63	0.8310	7.57	2.33
+360°				29.46	0.8540	9.72	1.12

Another specimen of oil collected from a well in the same sandstone at Olive, Noble County, 8 miles north of Macksburg, where the oil rock is only 40 feet below the bed of the creek, gave as its specific gravity, a value somewhat larger than the other, 0.8241. A determination of nitrogen in this oil gave 0.0293.

For an examination of oil from the 300-foot sand, a specimen was taken from a well on the farm of J. McLauth, one mile south of Macksburg. A small pocket of oil was opened in this sand, but it was soon exhausted, and the well continued to the Berea Grit. This oil had a peculiar reddish tinge that is frequently observed in petroleum from this sand. As will be seen in the following table it differs essentially in its composition and physical characteristics from the 140-foot oil :

Crude oil	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-Absorp.	HBr set free.
	84.45	13.79	0.018		0.8205	8.45	2.35
60–85°				0.55		0.00	0.00
85–110°				2.70		1.50	0.25
110–135°				3.50		3.03	1.17
135–160°				7.37	0.740	3.52	1.39
160–185°				5.96	0.771	3.88	1.37
185–210°				3.50		5.20	1.13
210–235°				6.66	0.789	5.75	1.93
235–260°				4.89		8.09	2.49
260–285°				7.37	0.811	8.66	2.44
285–310°				4.89		9.42	2.76
310–335°				3.50		11.70	3.97
235–260°				18.59	0.827	17.01	5.63
+360°				28.05	0.891	18.54	6.07

Quantities of oil were taken from Wells Nos. 6 and 9 in the 500-foot sand on the farm of Mr. J. S. Dunn, situated 1½ miles north of Macksburg and 1 mile south of Dexter City.

This oil rock is here 450 feet deep, and these wells are 1600 feet apart. Well No. 9 was drilled between 1861 and 1865, in the early days of oil. It started at 100 barrels and is now running 3 barrels daily. Well No. 6 was drilled in 1889. It started at 125 barrels and is now running 10 barrels daily of a light green oil. The sandstone is here about 22 feet thick, and it varies between medium and coarse sand rock. The specific gravity of the oil from well No. 9 is 0.8067 and that

from well No. 6, 0.7971. The latter well is more nearly in the center of the deposit, which doubtless accounts for its lightness. An extended examination was made of the oil from well No. 6, with the following results:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	84.19	14.75	0.015		0.7971	9.46	2.64
35–60°				1.33		0.79	0.51
60–85°				3.33		1.19	0.90
85–110°				6.33	0.6970	1.82	0.87
110–135°				3.33		2.32	0.77
135–160°				6.00	0.7440	3.71	0.95
160–185°				4.00	0.7640	4.94	1.25
185–210°				7.33	0.7760	5.94	1.83
210–235°				3.33		6.66	2.37
235–260°				8.33	0.7990	7.76	2.06
260–285°				5.00	0.8160	9.18	2.58
285–310°				3.33		11.03	3.04
310–335°				2.67		10.98	3.74
335–360°				20.00	0.8270	24.84	4.53
+360°			0.033	23.34	0.8420	26.38	9.08

Petroleum from the 700-foot sand was obtained from well No. 1, on the Mosely form, 2 miles north of Macksburg and 1 mile east of Dexter City. This well was drilled in 1889, and the sand was reached at 725 feet. It started at 10 barrels aud flowed for some time, but now it yields 2–3 barrels daily and is pumped.

The following results were obtained in an examination of this oil:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	84.56	14.33	0.038		0.3138	5.93	1.91
60–85°				2.41		1.73	1.73
85–110°				3.45		2.92	2.22
110–135°				7.24	0.725	3.65	3.36
135–160°				7.59	7.752	4.04	1.47
160–185°				7.59	0.764	5.03	1.41
185–210°				5.52		5.64	2.08
210–235°				4.83		6.26	2.16
235–260°				5.86		8.54	2.22
260–285°				4.83		10.21	3.15
285–310°				4.45		9.38	2.43
310–335°				4.83		11.24	2.36
335–360°				13.74	0.816	18.00	3.23
+360°				26.21	0.885	21.84	3.48

This examination of the petroleums from the upper sandstones was undertaken with the hope that a better knowledge of their composition would be interesting in comparison with the composition and properties of the Berea Grit oil, and it seemed all the more inviting since one of us (O. C. D.), was able, through his interest in this oil territory, to procure authentic specimens of fresh oil from these several geological formations.

For the examination of the Berea Grit petroleum from the 1500-foot oil sand, three specimens of this oil were procured. One came from well No. 3, on the McLauth farm, one mile south of Macksburg, the second from well No. 1, on the Warren farm, five miles north of Macksburg, and the third from Archer's fork. The latter will be more fully described later. The well from which the first sample was taken was drilled by Mr. J. S. Dunn, in 1884. At a depth of 1400 feet the sandstone was reached, and it was found to have a thickness of 11 feet. The well started with a small volume of oil and 400,000 feet of gas daily, which still continues in smaller quantities.

After the well was torpedoed the yield of oil was one-fourth of a barrel daily, which still continues. This oil has a high specific gravity, 0.8622, doubtless due to the removal of the lighter portions by the gas.

The well from which the second specimen was collected was drilled in 1893. It started at a rate of 85 barrels daily from a depth of 1480 feet, and now yields 3 barrels. Like most wells drilled to the Berea Grit, sufficient gas escaped to cause the well to flow at first, but it soon had to be pumped. This oil was of a beautiful amber color and much lighter than the first. It gave the following results on examination:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	85.52	14.59	0.064		0.8274	9.96	3.47
35–60°				0.54		0.26	0.27
60–85°				1.08		0.54	1.08
85–110°				1.62		1.38	1.66
110–135°				3.70		2.76	1.81
135–160°				3.70		3.75	1.74
160–185°				5.55		5.14	1.48
185–210°				6.60		5.41	2.00

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
210–235°				3.70		8.00	2.60
235–260°				5.55		8.01	2.27
260–285°				5.55		9.29	2.48
285–310°				2.22		10.47	3.09
310–335°				2.22		10.82	3.09
335–360°				11.11	0.8320	17.60	6.01
+360°			0.167	46.29	0.8900	20.31	7.08

As we have observed in other instances, the nitrogen compounds remained almost entirely in the residue above 360°.

The third specimen of this oil was taken from well No. 1, on the J. W. Ward farm at Archer's Fork, Washington County, 20 miles from Macksburg, in the eastern extension of the Eureka field. This well was drilled by Barnsdale & Co., in 1890. The sandstone was reached at 1780 feet, and it was 14 feet thick at this point. At first the well flowed 250 barrels daily. It now yields 11 barrels.[1]

The geological formations and the individual strata encountered in sinking a well to the Berea Grit are very clearly explained by the record of a well drilled in March, 1895, by Mr. J. S. Dunn, 600 feet from the Ward well mentioned above. This well was started on a hill 181 feet above the level of the Ward well. It produced oil in small quantity, but it yielded 500,000 feet of gas daily.

The thickness of the different rock strata and the depths are as follows:

Rock formation.	Thickness in feet.	Depths.
Soil	8	8
Rock sand	10	18
Light slate	43½	61½
Soft red rock	43½	105
Mountain sand	50	155
Light slate / Level of Ward well	30	185
Red rock	40	225
Light slate	15	240
Red rock	7	247
Light slate	7	254

[1] In procuring for examination a quantity of oil from this well as a representative petroleum from the Berea Grit in the Eureka field we are indebted to the zealous interest of Mr. J. S. Dunn, who crossed the country in an indirect course on account of freshets, a distance of 30 miles, in order that we might have some of this oil in unquestionable purity.

Rock formation.	Thickness in feet.	Depths.
Dark slate	5	259
Coal	1	260
Red rock	10	270
Light slate	20	290
Red rock	10	300
Light slate Bottom of 10-inch casing	45	345
Slate	10	355
Red rock	90	445
Slate, water	60	505
Shales with sandstone Bottom of 8-inch casing	345	850
Sandstone, water First Cow Run sand	85	935
Slates	94	1029
Sand rock water Second Cow Run sand	67	1096
Slate	20	1416
Sandstones, light & dark	156	1272
Shale & shells of sandstone	50	1322
Lime and sandstones, bottom of 6-inch casing	23	1345
Sandrock, "Big Indian"	220	1565
Slate	20	1585
Sandrock, "Squaw"	15	1600
Cuyahoga shale	340	1940
Berea black shale	21	1961
Berea Grit, gas	8	1969
Bedford shale	30	2009

A specimen of gas was collected from well No. 8, on the J. S. Dunn farm, near Dexter City. This well was drilled in 1891. It started at 250 pounds of oil daily. The quantity of gas is not large but it contains a considerable proportion of illuminating hydrocarbons. The higher percentage of illuminating constituents in this gas is doubtless due to the fact that it came from an oil well. It was shown by analysis to have the following composition:

Carbonic dioxide	0.30
Carbonic oxide	0.40
Oxygen	4.00
Nitrogen	1.20
Illuminating hydrocarbons	2.60
Marsh gas	91.20
	99.70

A specimen of gas was also collected from well No. 1, on the Mitchell farm, on Buffalo Run. This well was the first to reach the Berea Grit. It has supplied Dexter City with gas for heating, lighting, and manufacturing during eight years. An analysis of this gas gave the following results:

Carbonic dioxide	0.10
Carbonic oxide	0.80
Oxygen	0.30
Nitrogen	1.00
Illuminating hydrocarbons	0.7
Marsh gas	97.0
	99.9

From his observations on the Alsace petroleum, Engler concluded that the specific gravity decreases with the depth of the well. This inference is not fully supported by our study of the sandstone oils of Southern Ohio. It is true that the lightest oil is found in the Berea Grit, but this stratum also contains the heaviest oil. The oil from the 500-foot sand is nearly as light as the Berea Grit 1500-foot sand. These differences will be apparent in comparing the specific gravity of the oils from the different sandstones:

	Specific gravity.
140-foot sand	0.8118
300 " "	0.8205
500 " "	0.7971
700 " "	0.8183
1500 " "	0.8274
" " "	0.7939

The percentages of the more volatile distillates increases with the depth of the well, except the heavier Berea Grit oil. As will be seen later, the largest quantity of volatile constituents are contained in the lighter Berea Grit oil.

From the following comparison of the percentages of nitrogen in the oils taken at different depths, it appears that the proportion of this element increases with the depths, although oil from the 140-foot sand contains more than those from the strata next below:

	Percentage of nitrogen.
140-foot sand	0.027
300 " "	0.018
500 " "	0.015
700 " "	0.038
1500 " "	0.064
" " "	0.036

The 10 gallons of Berea Grit oil which we obtained from the Ward well mentioned above was free from sediment, of a very light amber color, and second in quality only to the famous Pinesborough petroleum. It deposits paraffin in large quantity when cooled to 0°, and crystals appear even at 10°. The composition and properties of this oil are given in the following table:

Crude oil.	C.	H.	N.	Per cent. of dist.	Specific gravity.	Br-absorp.	HBr set free.
	84.35	14.72	0.038		0.7939	6.25	2.23
35–85°				0.66		0.00	0.00
85–110°				7.33	0.6570	0.00	0.00
110–135°				10.00	0.6790	1.56	0.42
135–160°				11.66	0.7393	1.63	1.54
160–185°				7.00	0.7568	2.46	1.58
185–210°				7.00	0.7710	3.54	1.94
210–235°				5.33	0.7904	4.32	3.41
235–260°				5.33		6.31	2.94
260–285°				5.33	0.8127	7.58	3.07
285–310°				5.33		9.60	2.83
310–335°				5.00	0.8288	9.09	3.59
335–360°				4.00		13.59	3.56
+360°				25.00	0.8756	16.89	5.01

As shown in another paper, from conclusions based in part upon results herein described, it is evident that cracking during distillation, begins in these oils at temperatures varying between 185° and 235°. It is still somewhat uncertain, however, to what extent the increase in bromine-absorption is dependent upon normal constituents of the crude oil with an absorptive capacity, and to what extent upon decomposition-products of the distillation.

On account of the very large proportion of the volatile distillates in the Berea Grit oil, it would have been interesting to separate the more volatile hydrocarbons for the purpose of identifying them, and comparing them with the correspond-

ing constituents of Pennsylvania, Ohio, Trenton, and Canadian corniferous, limestone oils, which one of us (C. F. M.) has under investigation. But unfortunately this oil is not refined separately, and to collect the more volatile portions, a larger quantity of the crude oil must be distilled than can be done outside of a refinery. We have assumed, therefore, that these portions have the same composition as those of Pennsylvania petroleum, and we have directed our attention to the less volatile portions of this oil. The 10 gallons of crude Berea Grit oil already mentioned, was separated into 25°, 10°, 5°, and 1° fractions, and distillation of these portions continued under a constant tension of 730 mm., maintained by means of the regulator elsewhere described.[1] The fractions began to collect after the tenth distillation, but much longer distillation was necessary for the separation of the constituents, as well as to show that the intermediate fractions were mixtures of higher and lower products. The quantities collected between 150° and 158° were small. At 159–160° the fractions were sufficiently large to indicate the presence of a single body. On the basis of the statement of Pelouze and Cahours[2] that a decane $C_{10}H_{20}$, boiling-point 161–162°, is contained in Pennsylvania petroleum, all works on organic chemistry mention decane as a constituent of petroleum. The Organic Chemistry by Beilstein, 2d edition, states that the decane found by Pelouze and Cahours, boiling-point 161°, is probably normal decane.

Nevertheless the work of Pelouze and Cahours was not sufficiently thorough to inspire full confidence that they really had in hand a decane. Then other results seemed to disprove the presence in petroleum of a decane with this boiling-point. On this account we have given particular attention to this distillate in the oils now under examination. The fraction 159–160° from Berea Grit petroleum was submitted to prolonged distillation to ascertain beyond question whether the considerable quantities collecting at this point could be subdivided. After the twentieth distillation, however, the quantity at this point remained practically constant, and it

[1] This JOURNAL, 17, 723; and Proc. Amer. Acad., 31, 10.

[2] Ann. Chim. Phys. [4], 1, 5.

repeatedly distilled at 162–163°, tension 760 mm. Since other oils gave a similar result, even after the fiftieth distillation, it must be assumed that American petroleums contain a hydrocarbon with this boiling-point.

The following analyses were made of the distillate 162–163° from Berea Grit petroleum after drying over sodium :

0.1514 gram of the oil gave 0.4732 gram CO_2, and 0.1979 gram H_2O.

	Calculated for $C_{10}H_{20}$	$C_{10}H_{22}$.	Found.
C	85.71	84.51	85.25
H	14.29	15.49	14.53

The specific gravity of the unpurified distillate at 20° was 0.7629.

A portion of this distillate was heated gently for some time with fuming sulphuric acid. At first it became slightly warm when shaken with the acid, probably on account of the reaction on the aromatic hydrocarbons. The diminution in weight by the action of the acid was equivalent to two per cent. of the weight taken. Evidently the action of the acid consisted merely in removing mesitylene, boiling-point 163°, with which this distillate was contaminated. Indeed, the presence of the latter body was shown by the formation of a barium salt of the sulphonic acid formed by the action of fuming sulphuric acid. Upon neutralizing the acid solution with baric carbonate and evaporating to dryness, a barium salt was obtained, sparingly soluble in water, and crystallizing in clusters of needles.

0.5693 gram of the salt thus obtained lost nothing on standing over sulphuric acid, nor when heated to 100°, but on ignition with sulphuric acid 0.2564 gram of baric sulphate was obtained.

Calculated for $(C_9H_{11}SO_3)_2Ba$.	Found.
25.61	26.45

The purified distillate gave the following results on analysis :

I. 0.1513 gram of the oil gave 0.4691 gram CO_2, and 0.2070 gram H_2O.

II. 0.1545 gram of the oil gave 0.4786 gram CO_2, and 0.2130 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	Found. II.
C	84.51	84.57	84.29
H	15.49	15.21	15.24

A determination of the specific gravity of the purified oil gave 0.7475 at 20°.

A determination was also made of the vapor density. 0.1436 gram of the oil gave 69 cc. of vapor at 182°, and under a tension of 395.5 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.90	5.15

The boiling-point of this distillate was scarcely changed by treated with the acid. It nearly all distilled between 162° and 163°. Its odor was very faint, resembling that of the petroleum hydrocarbons in general. Like other hydrocarbons which we have separated from contaminating bodies, sodium remained untarnished in it after standing.

The quantity of the distillates were small above this point to 168°, but between this limit and 173° larger amounts collected, which by further distillation gave 95 grams, which all came over at 174–175°, under a tension of 760 mm. and with the mercury all in the vapor.

One portion (*a*) of this oil was reserved for determinations of carbon and hydrogen, without further treatment. Another portion (*b*) was shaken with concentrated sulphuric acid until a fresh acid produced no coloration. A third portion (*c*) was allowed to stand twenty-four hours with occasional shaking with a mixture of concentrated nitric and sulphuric acids. The latter treatment caused the separation in small quantity of a yellow oil that deposited crystals on standing. After crystallization from alcohol, in which it is rather sparingly soluble, this substance melted at 183–184°, showing it to be trinitropseudocumol, melting-point 185°. It was evidently formed from a small amount of cumol which still remained in this fraction. Another portion of the same product was gently heated during twelve hours with the mixture of acids. A vigorous action set in soon after heat was applied, as should be expected,

followed by complete decomposition of more than fifty per cent. of the oil. After a second treatment the oil disappeared entirely and in its place was a black porous solid, insoluble in water, but soluble in alcohol. Evaporation of the alcohol left a thick oily residue, from which no definite product could be separated. During the action of the acid a sublimate formed in the tube of the condenser that gave off the characteristic fumes of nitric dioxide when treated with water. This snbstance gave an acid reaction, and its color resembled that of butyric acid. The black solid formed by the action of the acid mixture had a similar odor. When treated with baric carbonate, a barium salt was formed with effervescence, and upon evaporation a crystalline salt separated, but not in sufficient quantity for analysis. In respect to its behavior toward the action of these acids, this oil resembles the corresponding fractions of other petroleums which are now under examination in this laboratory. Without further purification, carbon and hydrogen were determined in (*a*) with the results given below. For Analysis I the oil was dried over calcic chloride, and for Analyses II and III it was dried over sodium; as in all crude distillates, sodium caused a heavy flocculent, yellow precipitate to separate, which doubtless affected the proportions of carbon and hydrogen.

I. 0.1434 gram of the oil gave 0.4523 gram CO_2, and 0.1878 gram H_2O.

II. 0.1420 gram of the oil gave 0.4425 gram CO_2, and 0.1904 gram H_2O.

III. 0.1538 gram of the oil gave 0.4830 gram CO_2, and 0.2026 gram H_2O.

	Calculated for		Found.		
	$C_{10}H_{22}$.	$C_{10}H_{20}$.	I.	II.	III.
C	84.51	85.71	86.02	84.92	85.65
H	15.49	14.29	14.55	14.90	14.64

A determination of the specific gravity of this fraction at 20° gave 0.7624.

In a determination of its vapor density by the Hofmann method, 0.1628 gram of the oil gave 78 cc. of vapor at 182°, and under a tension of 417.1 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.93

In a second portion (*b*) of the same fraction that had been treated with sulphuric acid, carbon and hydrogen were also determined.

I. 0.1652 gram of the oil gave 0.5199 gram CO_2, and 0.2136 gram H_2O.

	Calculated for $C_{10}H_{22}$.	$C_{10}H_{20}$.	Found.
C	84.51	85.71	85.83
H	15.49	14.29	14.37

The specific gravity of this oil at 20° was found to be 0.7607, showing that a heavier body had been removed by the acid.

In determining the vapor density by the method of V. Meyer, 0.0511 gram of the oil gave 8.8 cc. of air at 18.°5, and under a tension of 725 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	5.03

The third portion (*c*) of the fraction 173–174°, after long standing with a mixture of nitric and sulphuric acids, was boiled with sodium as long as a flocculent solid continued to separate. Its boiling-point was not changed by this treatment, but analysis showed an appreciable change in the percentages of carbon and hydrogen:

I. 0.1483 gram of the oil gave 0.4596 gram CO_2, and 0.2047 gram H_2O.

II. 0.1540 gram of the oil gave 0.4775 gram CO_2, and 0.2102 gram H_2O.

III. 0.1424 gram of the oil gave 0.4424 gram CO_2, and 0.1989 gram H_2O.

	Calculated for $C_{10}H_{22}$.	Found. I.	II.	III.
C	84.51	84.50	84.57	84.72
H	15.49	15.33	15.17	15.52

The specific gravity of this oil at 20° was found to be 0.7509.

In a determination of its vapor density, 0.1186 gram of the oil gave by the Hofmann method, 64 cc. of vapor at 182° and 370 mm.

Calculated for $C_{10}H_{22}$.	Found.
4.92	4.91

In a second determination of the vapor density in a portion of the fraction 173–174°, after warming with fuming sulphuric acid, the following results were obtained :

0.1397 gram of the oil gave 69.4 cc. of vapor at 182°, and under a tension of 386 mm.

Required for $C_{10}H_{22}$.	Found.
4.92	5.11

Carbon and hydrogen were also determined after treatment with fuming sulphuric acid.

I. 0.1529 gram of the oils gave 0.4743 gram CO_2, and 0.2113 gram H_2O.

II. 0.1600 gram of the oil gave 0.5000 gram CO_2, and 0.2230 gram H_2O.

	Calculated for $C_{10}H_{22}$	Found. I.	II.
C	84.51	84.63	84.69
H	15.49	15.36	15.40

The specific gravity of this oil at 20° was found to be 0.7517, practically the same as the product purified with nitric and sulphuric acids.

Since, after the tenth distillation, considerable quantities of distillates collected between 180° and 185°, distillation of the single degree fractions between 174° and 185° (tension 173 mm.) was continued until only small quantities remained within these limits. The bearing of this observation on the results of Pelouze and Cahours, and of Warren in similar fractions from Pennsylvania petroleums, and of Markownikoff in Russian oil, will be more fully considered in connection with the results of work now in progress on the other oils.

After the thirteenth distillation, 110 grams collected at 190–191° (tension 730 mm.), which distilled at 194–196°, nearly all at 195° (tension 760 mm.), with the mercury column wholly in the vapor. An analysis without further treatment gave the following results :

I. 0.6366 gram of the oil gave 0.4250 gram CO_2, and 0.1826 gram H_2O.

II. 0.1504 gram of the oil gave 0.4659 gram CO_2, and 0.2044 gram H_2O.

III. 0.1656 gram of the oil gave 0.5184 gram CO_2, and 0.2166 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.	III.
C	84.62	85.02	84.55	85.35
H	15.38	14.86	15.11	14.53

The oil used for Analysis I was dried over calcic chloride, while that used in Analyses II and III was dried over sodium.

In drying this distillate over sodium a heavy flocculent precipitate separated, probably formed by the decomposition of unstable constituents.

The specific value of the unpurified fraction at 20° was found to be 0.7802.

A determination of its vapor density by the method of V. Meyer, gave the following values:

I. 0.1383 gram of the oil gave 20.9 cc. at 16°, and a tension of 732.1 mm.

II. 0.1473 gram of the oil gave 22.8 cc. of the vapor at 19.5°, and a tension of 715.6 mm.

Calculated for $C_{11}H_{24}$.	Found. I.	II.
5.31	5.62	5.68

A portion of this distillate was next shaken with concentrated sulphuric acid until agitation with fresh acid produced no coloration. The oil was washed with sodic hydrate and water, and dried for analysis:

I. 0.1478 gram of the oil gave 0.4580 gram CO_2, and 0.2036 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found.
C	84.62	84.59
H	15.38	15.32

In a determination of its specific gravity the same oil gave at 20°, 0.7696.

Another portion of the same fraction was allowed to stand with occasional shaking twenty-four hours with a mixture of concentrated sulphuric and nitric acids. The washed and dried oil was boiled with sodium as long as it gave a flocculent precipitate. By this treatment neither the percentage composition nor the boiling-point was appreciably changed:

I. 0.1476 gram of the oil gave 0.4575 gram CO_2, and 0.2021 gram H_2O.

II. 0.1507 gram of the oil gave 0.4664 gram CO_2, and 0.2086 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.
C	84.62	84.53	84.41
H	15.38	15.22	15.38

The specific gravity of this oil at 20° was found to be 0.7622.

In a determination of its vapor density by the method of V. Meyer, 0.1372 gram of the oil gave 20.5 cc. of vapor at 16°, and 734.3 mm.

Calculated for $C_{11}H_{24}$.	Found.
5.31	5.67

After treatment of another portion of this fraction with fuming sulphuric acid, the percentages of carbon and hydrogen were slightly affected.

I. 0.1532 gram of the oil gave 0.4753 gram CO_2, and 0.2131 gram H_2O.

II. 0.1503 gram of the oil gave 0.4648 gram CO_2, and 0.2108 gram H_2O.

	Calculated for $C_{11}H_{24}$.	Found. I.	II.
C	84.62	84.61	84.35
H	15.38	15.45	15.59

The oil treated with fuming sulphuric acid gave 0.7615 at 20°, as its specific gravity, a volume somewhat lower than the portion treated with the mixture of acids.

In continuing the distillation above this point no fractions collected in any considerable quantity below 208°. At 208–210° corresponding to 215°, at 760° a distillate collected, which without further purification, was analyzed.

I. 0.1475 gram of the oil gave 0.4638 gram CO_2, and 0.1895 gram H_2O.

II. 0.1490 gram of the oil gave 0.4660 gram CO_2, and 0.1926 gram H_2O.

	Calculated for $C_{12}H_{26}$.	Found. I.	II.
C	84.71	85.74	85.29
H	15.29	14.28	14.84

After treating this oil with concentrated sulphuric acid, the percentages of carbon and hydrogen were not materially changed.

I. 0.1479 gram of the oil gave 0.4615 gram CO_2, and 0.1975 gram H_2O.

II. 0.1530 gram of the oil gave 0.4794 gram CO_2, and 0.2009 gram H_2O.

	Found.	
	I.	II.
C	85.09	85.45
H	14.84	14.55

To a second portion of the distillate a mixture of nitric and sulphuric acid were added and allowed to stand, with occasional shaking.

In the treatment of all these distillates in this manner, a heavy oil invariably separated, the nitro compound of the aromatic hydrocarbon with a boiling-point near that of the principal constituent. In some instances the oil crystallized, but the quantities were insufficient to identify the product. In other oils these aromatic hydrocarbons are receiving more attention.

The oil treated with the acid mixture was boiled with sodium until it produced no further decomposition. Although the boiling-point was not materially changed, the percentages of carbon and hydrogen were sensibly affected.

0.1524 gram of the oil gave 0.4745 gram CO_2, and 0.2114 gram H_2O.

	Calculated for $C_{13}H_{28}$.	Found.
C	84.71	84.94
H	15.29	15.42

Another portion of this distillate was warmed for some time with fuming sulphuric acid, washed and dried for analysis.

I. 0.1479 gram of the oil gave 0.4595 gram CO_2, and 0.2002 gram H_2O.

II. 0.1511 gram of the oil gave 0.4705 gram CO_2, and 0.2095 gram H_2O.

	Calculated for $C_{13}H_{28}$.	Found.	
		I.	II.
C	84.71	84.72	84.92
H	15.29	15.04	15.40

In a determination of its specific gravity this oil gave 0.7746.

In a former paper allusion was made to the difficulty in removing water from the crude oils. This hygroscopic character seems to be an inherent quality of the individual hydrocarbons, which is perhaps more marked in those with higher boiling-points. It is difficult to remove moisture with fused calcic chloride so that it will not appear in the analysis. However long the oil stands with that drying agent, when brought in contact with metallic sodium, hydrogen is freely evolved. Even when carefully dried with sodium, if the oil is allowed to stand exposed to the air not longer than in redistillation, moisture is rapidly absorbed. Frequently drops of moisture appear after a time on the inside of the bottle, probably on account of changes in temperature. In combustions great care is necessary to maintain the temperature sufficiently high to burn the gases completely, and also to maintain a moderate rate, otherwise some gas escapes combustion. These peculiarities of the hydrocarbons were not fully appreciated until many analyses had been made and repeated.

It cannot be assumed that the oils prepared for analysis in this paper are products of decomposition by the methods of treatment, since no vigorous action was observed unless the solution was strongly heated. Fuming sulphuric acid at first caused a slight rise in temperature, doubtless on account of its action on the aromatic hydrocarbon. By vigorous boiling with nitric and sulphuric acids together, any of these oils may be completely decomposed with the formation of gaseous products, and the same is true of all petroleum distillates so far as we have examined them. In all this work the greatest care has been exercised to avoid, so far as possible, decomposition of the principal constituents.

On comparison of the percentages of carbon and hydrogen in the distillates described above, it is evident that the differences in composition of different homologues are not sufficient to distinguish between members of the series closely related. But the results of analysis are sufficiently well defined to distinguish between the series C_nH_{2n+2}, and the series C_nH_{2n}, or other series more remote.

In other oils now under examination the work is sufficiently advanced to show that the results described in this paper will be confirmed. Further discussion relating to the composition of these portions of American petroleum is reserved until the observations on other distillates are ready for publication.

A METHOD FOR THE STANDARDIZATION OF POTASSIUM PERMANGANATE AND SULPHURIC ACID.

By H. N. Morse and A. D. Chambers.

If potassium permanganate of normal composition can be obtained in a sufficiently pure condition, it should be practicable, by means of a standard solution of it and by use of a neutral reducing agent like hydrogen superoxide, to determine the strength of a dilute sulphuric acid, and, conversely, by means of a standard sulphuric acid to standardize a solution of potassium permanganate.

We have found the method here suggested very expeditious and quite as accurate as the methods usually employed for the standardization of these substances. For the formal comparison, the following reagents were prepared: dilute solutions of sulphuric acid and potassium permanganate, a neutral solution of hydrogen superoxide, pure oxalic acid, and pure potassium tetroxalate.

The concentration of the sulphuric acid was determined gravimetrically by precipitation as barium sulphate. Fifty cubic centimeters of it were found to contain 0.223 gram of the acid.

The solution of permanganate was made from the recrystallized salt, and was filtered through asbestos to remove suspended oxides of manganese. Fifty cubic centimeters of it contained 0.1626 gram of the salt, $KMnO_4$, according to a determination of its concentration by weighed quantities of potassium tetroxalate, and 0.1628 gram according to a similar determination by means of oxalic acid.

The potassium tetroxalate employed in standardizing the permanganate was prepared in the following manner: Nearly pure oxalic acid was dissolved in distilled water free from ammonia. Slightly less than one-fourth part of the solution

was exactly neutralized with potassium carbonate made from cream of tartar. The solution of neutral potassium oxalate was then poured into that of oxalic acid. After concentration by evaporation, the crystallized tetroxalate was separated from the mother-liquor, and further purified by recrystallization from water.

The oxalic acid, which was also used to determine the strength of the permangate, was recrystallized, first from a mixture of equal parts of alcohol and ether, and afterwards repeatedly, from water. The oxalic acid and the potassium tetroxalate were compared with each other, and with other acids of known concentration, and were found to have the normal neutralizing power.

The hydrogen superoxide used was the ordinary commercial solution. To render it neutral, it was agitated with zinc oxide, which had been heated in a muffle, and then filtered through asbestos.

Experiment I.

Determination of the Strength of the Permanganate by Means of the Standard Sulphuric Acid.—A considerable excess of the sulphuric acid was measured into a beaker and treated with a small quantity of hydrogen superoxide. Permanganate was then added from a burette, as long as the color disappeared. Afterwards more of the superoxide was introduced and the titration with permanganate resumed. The repitition of this process was continued until about 50 cc. of the permanganate had been reduced, leaving in the solution a minute excess of the hydrogen superoxide. Finally, the acid remaining free was determined by means of a tenth-normal solution of ammonia, using litmus as the indicator. The quantity of permangate found in 50 cc. of the solution (calculated according to the equation $2KMnO_4 + 5H_2O_2 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 8H_2O + 5O_2$) was 0.1626 gram; while, as previously stated, the quantities found by potassium tetroxalate and oxalic acid were 0.1626 and 0.1628 gram respectively.

Experiment II.

Determination of the Strength of the Acid.—A new solution of potassium permanganate was prepared, and its concentra-

tion determined, as in the previous case, by means of potassium tetroxalate and oxalic acid. By the former, 50 cc. were found to contain 0.1743 gram of $KMnO_4$, and by the latter 0.1744 gram. The sulphuric acid was the same as that used in the first experiment. Proceding as previously described, and regarding 50 cc. of the permanganate as containing 0.17435 gram of $KMnO_4$, 50 of the acid were found to contain 0.223 gram of sulphuric acid, a result identical with that obtained when its concentration was determined by precipitation as barium sulphate.

The figures here given are in each case the mean of several determinations. The graduated apparatus used in the work was calibrated according to the system recently described,[1] which permits of the accurate measurement of liquids to the hundredths of a cubic centimeter.

Contributions from the Chemical Laboratory of Harvard College.

XCII.—SOME DERIVATIVES OF UNSYMMETRICAL TRIBROMBENZOL.[2]

By C. Loring Jackson and F. B. Gallivan.

The study of the behavior with various reagents of aromatic compounds containing bromine and nitro groups has been carried on for some years in this laboratory, but the greater part of the work has been devoted to derivatives of symmetrical tribrombenzol. It seemed of interest, therefore, to investigate on the same lines nitro compounds derived from unsymmetrical tribrombenzol. Of these compounds the tribromdinitrobenzol, melting at 135°, seemed the most promising, but before taking up the study of its behavior, it was necessary to determine its constitution, for, although the constitution usually assigned to it (Br1, Br2, $NO_2$3, Br4, $NO_2$5) was the most probable, it did not rest on an experimental basis. For this purpose, it was reduced with tin and hydrochloric acid, when a monobromphenylene diamine, melting at 93–94°, was obtained, which was converted by bromine water into a tetrabromphenylene diamine, melting at 213°. As this same

[1] This Journal, **16**, 479. (Note—Attention is called to an error which escaped the notice of the proof reader. The formula on page 479 should read $V = P\frac{p}{d}$.)

[2] Presented to the American Academy of Arts and Sciences, May 8, 1895.

monobromphenylene diamine has been made in this laboratory from tetrabromdinitrobenzol, in which the two nitro groups are in the meta position to each other, this proves that tribromdinitrobenzol, melting at 135°, has the constitution Br1, Br2, $NO_2$3, Br4, $NO_2$5, usually ascribed to it.

When this tribromdinitrobenzol is treated with aniline, two of the atoms of bromine are removed, and a bromdianilidodinitrobenzol melting at 191–192° is formed. This is what would be expected, as only two of the atoms of bromine which it contains are in positions favorable to renewal, (one ortho para, the other diortho to the nitro groups), while the third, (meta to the nitro groups) would be removed, if at all, only by more violent action. It resembles in this respect, therefore, tribromtrinitrobenzol, which with aniline gives trianilidotrinitrobenzol.

The behavior of the tribromdinitrobenzol 1, 2, 4, 3, 5 with sodic ethylate brings out still more strongly the similarity between this substance and tribromtrinitrobenzol. With this latter body two reactions take place simultaneously, one consisting in the replacement of the three atoms of bromine forming trinitrophloroglucine triethylether, the other in that of two nitro groups forming tribromdinitroresorcine, diethylether.[1] In the same way the action of sodic ethylate upon this tribromdinitrobenzol gives two or more organic products, one a bromdinitrophenol, melting at 67°, formed by replacing the two more loosely attached atoms of bromine by ethoxy radicals, and another, a tribromresorcine diethylether, melting at 158°, and formed by the replacement of the two nitro groups by ethoxy radicals. On one occasion a small amount of a third organic product was obtained, but not enough for identification. In these experiments, therefore, the bromine atom, which was meta to the two nitro groups, behaved like the third nitro group in tribromtrinitrobenzol, in this respect resembling the similarly placed atom of bromine in tetrabromdinitrobenzol.[2] It, is, however, strange that the two ethoxy groups should have replaced the two nitro groups leaving the bromine atom unaffected, especially as in the case of tetrabromdinitrobenzol, one nitro group and the bromine

[1] Proceedings Amer. Acad., **27**, 283. [2] *Ibid.*, **24**, 293.

atom are replaced in the parallel reaction. It is possible that the third product, which we could not obtain in a quantity sufficient to identify, was a dibromnitroresorcine diethylether formed in this way, but, if this were the case, the reaction was a very subordinate one.

The action of sodium malonic ester on this tribromdinitrobenzol gave a trace of a red sodium salt, but we have not succeeded in modifying the conditions of the reaction so to as obtain enough of this product even for purification. The failure to obtain this reaction, we regret the more, because the study of this case promised to throw light on the strange replacement of bromine by hydrogen in nitrobrombenzols, which has been a subject of study for many years in this laboratory.

In addition to the work just summarized we have determined the constitution of the tetrabrombenzol melting at 175°, a substance which was usually considered symmetrical, although this conclusion was not based on experimental grounds. We have done this in two ways: First, by replacing the nitro group in the tribromnitrobenzol, melting at 93°, by bromine directly, that is, by heating it with bromine and water; and second, by converting this same tribromnitrobenzol into the corresponding tribromaniline, and replacing the amido group by a bromine atom by means of Griess's reaction. In both cases the product was the tetrabrombenzol, melting at 175°, and as this tribromnitrobenzol has the constitution Br1, Br2, Br4, $NO_2$5, it follows that this tetrabrombenzol really has the symmetrical constitution usually attributed to it.

The new tribromaniline ($NH_2$1Br2, Br4, Br5,) made in the course of this work melts at 80°, its acetanilide at 188°. It differs from the ordinary tribromaniline also in that it forms salts with greater ease. Its chloride, bromide and sulphate were prepared and analyzed.

An attempt to prepare nitro compounds from the symmetrical tetrabrombenzol did not lead to the desired result, the product being hexabrombenzol.

Some attempts were also made to prepare the adjacent tetrabrombenzol, but our work in this direction is so far from fin-

ished that the publication of it must be postponed for the present.

Preparation of Tribrombenzol (1, 2, 4).

After trying a number of the methods recommended for making unsymmetrical tribrombenzol, we finally adopted that from dibromacetanilide given by Griess,[1] and also used by Körner,[2] which after a few modifications gave satisfactory results. We proceeded as follows: Fifty grams of acetanilide suspended in five liters of water were treated with a stream of air loaded with bromine vapor, until the acetanilide was converted into a reddish-brown oil. A smaller amount of water must not be used, as in that case tribromaniline was formed in considerable quantity. This may have been due to a partial saponification of the acetanilide by the hydrobromic acid formed in the process. The red oil obtained in the way described was treated with dilute sodic hydrate, when it solidified, and, after a thorough washing with water, was boiled under a return condenser with dilute sulphuric acid of specific gravity 1.44, until all the organic matter had dissolved. As the solution cooled, fine crystals of the sulphate of dibromaniline separated, which were filtered from the large excess of sulphuric acid and then suspended in water acidified with sulphuric acid, and converted into the diazo compound by adding a little more than the calculated amount of sodic nitrite; as the diazo compound is formed the crystals go into solution. Bromine and potassic bromide were then added, forming a yellow precipitate of dibromdiazobenzol perbromide, which was filtered out, dried on filter-paper and decomposed by warming it with glacial acetic acid. On cooling the solution deposited the tribrombenzol as an oil, which solidified on standing and melted at the proper temperature, 44°. In this way five grams of tribrombenzol were obtained from five grams of dibromaniline, instead of 5.8 grams, that is, 86 per cent. of the theoretical yield. The dibromaniline could also be converted into tribrombenzol to advantage by carrying on the Griess reaction in a concentrated solution of hydrobromic acid, and disregarding the yellow precipitate of dibromdiazo-

[1] Jahresb., 1866. 454. [2] Gaz. Chim., 4, 405.

benzol bromide, distilling with an additional quantity of concentrated hydrobromic acid. Both these processes give better results than the decomposition of the perbromide with sodic carbonate or alcohol, which yielded considerable amounts of tarry impurities, or than the Sandmeyer reaction, from which we did not succeed in getting a good yield.

Constitution of Tribromdinitrobenzol, Melting at 135°.

Before studying the behavior of this substance it was necessary to establish its constitution, which had not yet been done experimentally; although there could be little doubt as to its graphic formula, because the unsymmetrical tribrombenzol gives by the action of nitric acid two mononitro derivatives, which have been proved to have the constitutions Br1, Br2, Br4, NO_25, and Br1, Br2, NO_23, Br4 respectively,[1] and it is probable, therefore, that the dinitro compound obtained by the more energetic action of nitric acid has the constitution Br1, Br2, NO_23, Br4, NO_25. To settle the point definitely we submitted the tribromdinitrobenzol, melting at 135°, to reduction. Ten grams of this substance, moistened with a little alcohol, were allowed to stand with a mixture of tin and hydrochloric acid. The color changed quickly from yellow to grayish white, and at the end of fifteen minutes the gray solid dissolved with a slight rise in temperature. The liquid poured off from the tin was then treated with an excess of sodic hydrate, until the precipitate of hydrate of tin had dissolved completely. The undissolved substance was filtered out and crystallized from a mixture of alcohol and ligroïn until it showed the constant melting-point 93–94°. This melting-point is the same as that of the monobromphenylene diamine obtained by Calvert and one[1] of us by the reduction of the tetrabromdinitrobenzol, melting at 227°. To characterize this substance still more certainly, it was treated with bromine water, as this reagent converts the monobromphenylene diamine (from tetrabromdinitrobenzol) into tetrabromphenylene diamine, melting at 214°. By this treatment with bromine water our substance gave a product which after purification

[1] Körner. Gaz. Chim., 4, 413.

by crystallization from a mixture of chloroform and alcohol, melted at 213° and gave the following result on analysis:

0.2310 gram of the substance gave 0.4088 gram of argentic bromide by the method of Carius.

	Calculated for $C_6Br_4(NH_2)_2$.	Found.
Bromine	75.47	75.34

These observations prove that the reduction products of tetrabromdinitrobenzol and of tribromdinitrobenzol, melting at 135°, are identical, and as the two nitro groups in the former substance are in the meta position, it follows that the two nitro groups in the tribromdinitrobenzol, melting at 135°, must also be in the meta position to each other, and that this substance has the constitution usually assigned to it Br1, Br2, $NO_2$3, Br4, $NO_2$5.

Behavior of Tribromdinitrobenzol (1, 2, 4, 3, 5,) with Aniline.

Two grams of tribromdinitrobenzol, when mixed with an excess of aniline, went into solution in a short time. To make certain that the reaction was complete, this solution was warmed for a minute or so on the steam bath. The excess of aniline was then removed by the addition of dilute nitric acid, followed by thorough washing with water, and the undissolved portion recrystallized from a mixture of benzol and alcohol, until it showed the constant melting-point 191–192°, when it was dried at 100° and analyzed with the following results:

I. 0.2216 gram of the substance gave by the method of Carius 0.0991 gram of argentic bromide.

II. 0.2017 gram gave 0.0891 gram of argentic bromide.

	Calculated for $C_6HBr(C_6H_5NH)_2(NO_2)_2$.	Found.	
		I.	II.
Bromine	18.64	19.03	18.80

The substance was, therefore, formed by replacing two of the atoms of bromine by anilido groups, and is a bromdianilidodinitrobenzol.

Properties of Bromdianilidodinitrobenzol.—It crystallizes from a mixture of benzol and alcohol in yellowish orange needles

[1] Proc. Am. Acad., 31, 155.

in radiating groups, forming woolly masses. The crystals, when better developed, are slender prisms with square ends. It melts at 191° to 192°, and is slightly soluble in cold alcohol, more freely in hot; soluble in ether, chloroform, benzol, acetone; essentially insoluble in water. The best solvent for it is a mixture of alcohol and benzol. Hydrochloric acid has no apparent action on it. Nitric acid dissolves it, but the addition of water seems to precipitate the unaltered substance. Strong sulphuric acid also dissolves it, but on dilution the substance precipitated has a different color from that of the original bromdianilidodinitrobenzol.

Behavior of Tribromdinitrobenzol (1, 2, 4, 3, 5,) with Sodic Ethylate.

Thirteen grams of tribromdinitrobenzol were dissolved in benzol and mixed with an alcoholic solution of sodic ethylate containing four molecules of the ethylate to each molecule of the tribromdinitrobenzol. The solution turned yellow at first, and this color gradually changed to a brownish red. To complete the reaction it was allowed to stand at ordinary tempertures over night, when it was found that a considerable amount of solid matter had been precipitated. This was filtered out and proved to be mostly inorganic salts; its solution in water gave good tests for sodic nitrite and sodic bromide. The filtrate from these salts was allowed to evaporate spontaneously, the dark-colored residue thoroughly washed with water and then crystallized from alcohol until it showed the constant melting-point 158°, when it was dried at 100° and analyzed with the following result:

0.2430 gram of the substance gave by the method of Carius 0.3407 gram of argentic bromide.

		Calculated for $C_6HBr_3(OC_2H_5)_2$.
Bromine	59.55	59.67

The substance is, therefore, a tribromresorcine diethylether, formed by the replacement of the two nitro groups by two ethoxy radicals.

Properties of Tribromresorcine Diethylether.—It crystallizes from alcohol in long, white pearly plates terminated by two

planes at an acute angle, which is usually truncated by a basal plane. It has a disagreeable, rather characteristic odor and melts at 158°. It is nearly insoluble in cold alcohol, soluble in hot; soluble in chloroform, benzol or acetone; slightly soluble in cold ligroïn, more soluble in hot. The best solvent for it is hot alcohol.

The appearance of sodic bromide as one of the products of the reaction shows that this tribromresorcine diethylether could not be the only organic product of the action, and this second organic product was found in the aqueous wash waters used on the residue from the spontaneous evaporation of the organic solvents. The presence of this substance was indicated by the strong orange color of this aqueous solution. It was accordingly concentrated and acidified with dilute sulphuric acid, which precipitated an oil that usually remained obstinately liquid; even standing for two months did not bring it to crystallization, nor was treatment with sodic ethylate, precipitation of the salt formed with benzol, and setting free the phenol with sulphuric acid more successful. The precipitate was still oily. Finally a new preparation undertaken with great care, furnished us with some phenol which would crystallize. The preparation was carried on as follows: Ten grams of the tribromdinitrobenzol were dissolved in 100 cc. of benzol dried over sodium and mixed with an alcoholic solution of the sodic ethylate from two grams of sodium in a flask provided with a chloride of calcium tube. When the mixture had stood at ordinary temperatures over night it was acidified with dilute sulphuric acid and allowed to evaporate spontaneously, after which the residue was treated as before. The oily phenol obtained in this way soon crystallized in broad, thin scales, which melted at 67° after recrystallization from chloroform, and gave the following results on analysis:

0.1754 gram of the substance gave by the method of Carius 0.1162 gram of argentic bromide:

	Calculated for $C_6HBr(OH)_2(NO_2)_2$.	Found.
Bromine	28.67	28.20

It was formed, therefore, by the replacement of two of the bromine atoms by ethoxy radicals, which were afterward saponified to hydroxyls by a trace of moisture. From the experience obtained by work on related substances in this laboratory, we should infer that the two bromine atoms replaced were those in the ortho-para and diortho positions to the two nitro groups, and that, therefore, the substance is a bromdinitroresorcine, but this conclusion rests only on an analogy. If correct the substance is constituted as follows: Br1, OH_2, NO_2,3, OH_4, NO_2,5.

Properties of Bromdinitroresorcine.—It crystallizes from chloroform in broad, thin scales of slightly brownish color, which melts at 67°. It is very soluble in alcohol, ether, acetone or benzol; soluble in chloroform; insoluble in cold ligroïn, soluble in hot. With sodic hydrate it forms a soluble salt of a rather dark orange color.

On one occasion the reaction with sodic ethylate yielded a small quantity of a substance crystallizing in long needles and melting at about 80°, but, although we varied the conditions of the reaction in a number of ways, we have not succeeded in preparing this substance again, and therefore can give no account of its composition.

Behavior of Tribromdinitrobenzol (1, 2, 4, 3, 5,) with Sodium Malonic Ester.

Our experiments on this part of the subject led to no new compound. Ten grams of the tribromdinitrobenzol dissolved in absolute alcohol with a little benzol were mixed with 12 grams of malonic ester previously converted into sodium malonic ester, by treatment with an alcoholic solution of the sodic ethylate from 1.5 grams of sodium. After the mixture had stood for some time at ordinary temperatures, a dark red color had appeared, resembling that of the salts of other similar substituted malonic esters prepared in this laboratory. This seemed to indicate that the reaction had run in the desired way, but after the mixture had stood over night, and the product had been worked up in the usual manner more than 80 per cent. of unaltered tribromdinitrobenzol was recovered. Other experiments were then tried, allowing the mixture to

stand for several days; heating it, and even carrying on the experiment with amyl alcohol as the solvent at its boiling-point, but in every case most of the tribromdinitrobenzol was recovered unaltered. From all these experiments a very minute quantity of a substance was obtained, which behaved like a substituted malonic ester, since it gave a red solution with sodic hydrate, the color of which was discharged on acidification, but it was evident that it was not worth while to attempt to prepare enough of this substance for study.

Reduction of Tribromnitrobenzol (*1, 2, 4, 5.*)

Five grams of tribromnitrobenzol, melting at 93°, were moistened with a little alcohol and reduced with tin and hydrochloric acid by warming the mixture gently. The tribromnitrobenzol did not dissolve, but its yellow color gradually changed to gray, and when the reduction was complete the product was left as a grayish mass clinging to the tin. The liquid was filtered off, the residue washed thoroughly with water to remove stannous chloride and then purified by recrystallization from alcohol until it showed the constant melting-point 80°, when it was dried *in vacuo* and analyzed with the following results:

I. 0.3020 gram of the substance gave by the method of Carius 0.5165 gram of argentic bromide.

II. 0.2593 gram of the substance gave 0.4427 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_2$.	Found.	
		I.	II.
Bromine	72.73	72.79	72.66

The substance is, therefore, a new tribromaniline, and as it is made from the tribromnitrobenzol, melting at 93°, it must have the following constitution: Br1, Br2, Br4, $NH_2$5. It is worth mentioning that zinc dust and acetic acid did not reduce the tribromnitrobenzol.

Properties of Tribromaniline (1, 2, 4, 5.).—It crystallizes from alcohol in yellowish white, rather short needles, united longitudinally to form narrow plates with parallel sides and serrated or irregular ends. These plates are usually strongly

striated. It melts at 80°. It is very soluble in alcohol, ether, chloroform, or benzol; moderately soluble in cold ligroïn, soluble in hot; insoluble in water. It distils with steam, although with some difficulty. With acids it forms salts more easily than the ordinary tribromaniline (1, 3, 5, 2), since the chloride can be obtained by the long continued action of hot strong hydrochloric acid on the free base, and the sulphate by heating the base with strong sulphuric acid. The chloride, although soluble in cold water, is decomposed by hot water into hydrochloric acid and the tribromaniline. The most convenient method, however, for making the chloride or bromide is by passing the gaseous acid through a solution of the tribromaniline in benzol. The chloride, bromide and sulphate were studied more in detail, as described in the following sections.

Chloride of Tribromaniline (1, 2, 4, 5), $C_6H_2Br_3NH_2Cl$.—This salt could be made by heating the tribromaniline for some time with concentrated hydrochloric acid. The solid base slowly dissolved, forming a solution of the chloride. A much more convenient method, however, was that used by Gattermann[1] for making the chloride of the ordinary tribromaniline. Our tribromaniline was dissolved in benzol, and treated with gaseous hydrochloric acid, which gave a precipitate of the pure chloride.

0.5480 gram of the salt was dissolved in water, and after the base had been removed with ammonic hydrate, gave 0.2306 gram of argentic chloride.

	Calculated for $C_6H_2Br_3NH_2Cl$.	Found.
Chlorine	9.69	10.40

The chloride crystallizes from alcohol in white branching needles. It is soluble with some difficulty in cold water, but decomposed by hot water into tribromaniline and hydrochloric acid; soluble in alcohol or ether; insoluble in benzol.

Bromide of Tribromaniline, (1, 2, 4, 5,) $C_6H_2Br_3NH_2Br$.—This salt was formed like the chloride by passing gaseous hydrobromic acid through a benzol solution of the tribromaniline. It gave the following results on analysis:

[1] Ber. d. chem. Ges., **16**, 636.

0.4047 gram of salt gave after precipitation of the tribromaniline with ammonic hydrate, 0.1845 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_2SO$.	Found.
Bromine	19.47	19.41

The bromide resembles the chloride most closely in its properties.

Sulphate of Tribromaniline (1, 2, 4, 5,) $C_6H_2Br_3NH_2SO_4H$.—This salt was made by heating tribromaniline with strong sulphuric acid. It separated out from the acid as it cooled and was purified by crystallization from alcohol. It gave the following result on analysis:

0.2796 gram of the salt gave 0.1560 gram of baric sulphate.

	Calculated for $C_6H_2Br_3NH_2SO_4H$.	Found.
SO_4	22.43	22.94

The salt crystallizes from strong sulphuric acid in white plates; from alcohol in needles. It is rather soluble in water, very soluble in alcohol.

Tribromacetanilide, (1, 2, 4, 5), $C_6H_2Br_3NHC_2H_3O$.—Four grams of the tribromaniline were mixed with an excess of acetic anhydride and the mixture warmed on the water-bath until all the solid had dissolved, when it was treated with water, which threw down a voluminous precipitate. This, after recrystallization from alcohol until it showed the constant melting-point 188°, was dried at 100°, and analyzed with the following result:

0.2885 gram of the substance gave by the method of Carius 0.4390 gram of argentic bromide.

	Calculated for $C_6H_2Br_3NH_2C_2H_3O$.	Found.
Bromine	64.52	64.77

The substance is, therefore, a monacetyl compound, which is surprising, as Remmers[1] states he obtained a diacetyl derivative from the ordinary tribromaniline by the action of acetic anhydride.

Properties of Tribromacetanilide.—It crystallizes from alco-

[1] Ber. d. chem. Ges., 7, 350.

hol in white, woolly masses, which are seen under the microscope to be composed of radiating groups of branching needles, or, if very well developed, slender prisms with blunt ends. It melts at 188°; soluble in alcohol, ether, acetone, chloroform, benzol, or glacial acetic acid; insoluble in cold ligroïn, soluble in hot; insoluble in water. Alcohol or ligroïn is the best solvent for it. Fuming nitric acid converts it into a nitro compound, which was not further studied.

Constitution of Tetrabrombenzol Melting at 175°.

The constitution of this substance has never been determined experimentally, although it has been usually considered the symmetrical compound 1, 2, 4, 5. We have established its constitution by two different methods, both of which proceed from the tribromnitrobenzol, melting at 93°, which has the known constitution 1, 2, 4, 5.

First Method.—Five grams of tribromnitrobenzol, melting-point 93°, were mixed with bromine in slight excess over the amount necessary to give equal molecules of the two substances and with 2 cc. of water, and heated to 175–200° in a sealed tube for four hours. The product was washed with dilute sodic hydrate, and afterwards with water and then purified by crystallization from glacial acetic acid, when it showed the melting-point 173°, and gave the following result on analysis:

0.2143 gram of the substance gave by the method of Carius 0.4085 gram of argentic bromide.

	Calculated for $C_6H_2Br_4$	Found.
Bromine	81.21	81.13

These results leave no doubt that the substance is the tetrabrombenzol, although the melting-point is two degrees low, and as it is hardly possible that the reaction could be other than the replacement of the nitro group by an atom of bromine, proves that this tetrabrombenzol has the symmetrical constitution. It can be objected, however, that the reaction took place at a high temperature, 175–200°, which may have been enough to cause intramolecular transformation. Accord-

ingly we attacked the problem by another method, which was not open to this objection.

Second Method.—The tribromaniline already described in this paper, made by the reduction of the tribromnitrobenzol, melting at 93°, was converted into the sulphate of tribromdiazobenzol by treating it, suspended in dilute sulphuric acid, with the required amount of sodic nitrite. Bromine dissolved in potassic bromide was then added, and the heavy yellow precipitate of the diazoperbromide thus obtained was filtered out, dried as quickly as possible and decomposed by heating it with glacial acetic acid. On cooling the solution deposited beautiful white needles, which melted at 174–175°, and gave the following results on analysis :

0.2045 gram of the substance gave by the method of Carius 0.3890 gram of argentic bromide.

	Calculated for $C_6H_2Br_4$.	Found.
Bromine	81.21	80.95

This second method leads to the same conclusion as the first, and there can be no doubt that the tetrabrombenzol, melting at 175°, has the symmetrical constitution 1, 2, 4, 5.

We also attempted to make nitro compounds from the symmetrical tetrabrombenzol, in order to study their behavior with reagents, but without success. The symmetrical tetrabrombenzol, when boiled with fuming nitric acid alone, remains unchanged. When a mixture of fuming nitric acid and strong sulphuric acid was used, a white precipitate was obtained upon pouring the acid solution into water, which crystallized from benzol in long, silky needles, did not melt even when heated to 310°, but sublimed with tolerable ease. These properties indicated that the substance was hexabrombenzol, and this conclusion was confirmed by its analysis.

0.2152 gram of the substance gave 0.4413 gram of argentic bromide.

	Calculated for C_6Br_6.	Found.
Bromine	86.95	87.28

Riche and Berard[1] state that they obtained by the action of nitric acid on the tetrabrombenzol, melting at about 160°, a

[1] Ann. Chem. (Liebig), 133, 52.

mononitrotetrabrombenzol. We are inclined to think, in view of our experimental results, that this nitro compound may have been formed from some impurity in the tetrabrombenzol, since the melting-point ascribed to it is rather indefinite, but a more careful study of the subject will be necessary in order to explain satisfactorily these discordant results.

REVIEWS.

HELIUM.

A short review of the progress made in the investigation of the sources and properties of helium was recently published in this JOURNAL[1]; it is proposed in this second note to call attention to some of the work the records of which have been received since the earlier review was written.

Prof. Lockyer[2] seems to have been the first to show that "helium" from different sources exhibited spectroscopic differences, and that the so-called permanent lines of the solar chromosphere, at least in most cases, coincide with certain of the characteristic lines of helium. Deslandres also has shown[3] that but one of these permanent lines is absent from the spectrum of cleveite gas. Reports from various observers[4] have established the fact that the D_3 line of the chromosphere and the yellow line of cleveite gas are both double, the less refrangible being much the weaker of the pair in each case. Measurements of the distance between the lines would finally seem to have put beyond question the identity of solar and terrestrial helium.

At the meeting of the British Association, Lord Rayleigh reported upon the refractive indices and viscosities of argon and helium.[5] Compared with that of air taken as unity, the refractive index of the latter substance is but 0.146—by far the lowest yet reported. Dr. Gladstone announced that the specific refractive energy of argon, as deduced from Lord Rayleigh's results, indicates an element with an atomic weight of about 20 and not of about 40. This evidence would tend to offset that furnished by the ratio of the specific heats of argon and of helium.[6]

A very notable paper read at the same meeting was that of Profs. Runge and Paschen, of Hanover, on the spectra of

[1] Vol. **17**, 630. [2] Proc. Roy. Soc. **48**, 67, 113, 116, 192, 193; **49**, 1, 4.

[3] Compt. Rend. **120**, 1112, 1331.

[4] See, for example, Chem. News, **72**, 27; "Nature," **52**, 327, 458. For an adverse criticism on this view, see Wilde: Phil. Mag. **40**, 466.

[5] See "Nature," **52**, 533; Chem. News, **72**, 152.

[6] For an account of this discussion, see Chem. News, **72**, 223.

cleveite gas.[1] Earlier papers on the same subject had shown[2] that the spectrum of pure helium is absolutely free from any of the lines characteristic of argon, and that the spectra of two constituents are to be distinguished. In the present communication, after calling attention to the fact that by substituting in succession the numbers from 3 to 30, for m in the formula $\frac{m^2}{m^2-4}$, figures are obtained proportional to the wave-lengths of the visible lines of hydrogen, and that the formula $\frac{1}{\lambda} = A - \frac{B}{m^2} - \frac{C}{m^4}$ will enable one to calculate the wave-lengths of the members of a series of lines where two are known; they showed that whereas practically every element exhibits, a spectrum consisting of three series of lines, cleveite gas gives a spectrum containing six such series, and that these fall into two groups of three series each. Further, one of these groups has been seen without the other: one contains the "permanent" lines of the chromosphere, the other consists of lines only occasionally observed. One consists of double lines only—one of which, of course, is D_3,—the other of single lines. The average position—if such a phrase is permissible—of the lines of one group is farther towards the violet end of the spectrum and approaches that of the group of the lines of lithium; whereas that of the other group is nearer the average position of the lines of hydrogen. The conclusion to be drawn is therefore that cleveite gas contains two and only two constituents, one heavier than the other. By allowing the gas to flow through a porous plug into a vacuous sparking-tube, it was noticed that the spectrum first observed was almost exclusively that of the lighter, less refrangible constituent, and that D_3 and the other "permanent" lines made their appearance only gradually. The rule is thus borne out that the series of lines shift towards the violet as the atomic weight rises, provided the elements compared follow one another in a series of Mendeléeff's System. Since, from the determinations of the density of cleveite gas, the constituents may be assumed to have atomic weights between those of hydrogen and lithium, they would thus belong to the same series of the System and hence the denser—helium proper—would possess the more refrangible series of lines. A more recent communication[3] by the same authors points out that there are several lines noted by Crookes[4] in the spectra of specimens of "helium" exam-

[1] "Nature," **52**, 520; Chem. News, **72**, 181.

[2] Sitzb. Acad. Berlin, June 20 and July 11, 1895. For a translation of the second paper, see Phil. Mag. **40**, 297; Astrophys. J., January, 1896.

[3] "Nature," **53**, 245. [4] Chem. News, **72**, 87; "Nature," **52**, 428.

ined by him, which do not coincide with any of the lines thus far mapped by themselves as produced by cleveite gas.

Prof. Lockyer has discussed[1] the papers of Runge and Paschen and has pointed out where his own researches[2] had led him to similar conclusions as to the dual composition of cleveite gas.

Langlet has published[3] an account of experiments made upon the density of helium and upon the ratio of its specific heats. The former he finds to be 2.0 as compared with hydrogen as unity; the latter, 1.67—in close accord with the results obtained by Ramsay.

Olszewski has been unable[4] to produce the liquifaction of helium furnished him by Ramsay, even under the conditions which were successful in the case of hydrogen—*i. e.*, allowing the gas, under a pressure of 140 atmospheres, and cooled to —210° C., to expand suddenly.

Troost and Ouvrard maintain[5] that both argon and helium are completely absorbed when sparked in a tube furnished with magnesium terminals.

Helium appears to be a constituent of the gases contained in certain spring-waters,[6] and even, at times, of air.[6]

An examination of the coefficients of expansion of argon and helium as compared with those of air and hydrogen has been made by J. P. Kuenen and W. W. Randall.[7] The object in view was to determine what change occurred in the rate of expansion of the newly discovered gases as temperature rose, and thus to obtain evidence of any dissociation which might take place. A gas-thermometer filled with each of the four substances in turn was kept successively at some six or seven temperatures ranging between 0° and 281°, while the pressure required to keep the volume constant was carefully determined. The only change in the volume of the gas was that due to the expansion of the glass bulb. After making all the necessary corrections, the coefficient of expansion of argon between 0° and 100° was found to be 0.003668, and that of helium, 0.003665. No evidence of molecular change could be obtained, when the expansion of these gases was compared with that of air and hydrogen, at the boiling-points of chlorbenzene (132.1°), aniline (184.4°), quinoline (237.4°), and bromnaphthalene (280.4°).

[1] "Nature," **52**, 547. See also Chem. News, **72**, 271; "Nature," **53**, 167.
[2] *Loc. cit.* [3] Ztschr. anorg. Chem., **10**, 287; Chem. News, **72**, 259.
[4] "Nature," **52**, 544. [5] Compt. Rend., **121**, 394; Chem. News, **72**, 153.
[6] *Cf.* Compt. Rend. **121**, 392, 798, 819; Chem. News, **72**, 152, 223, 309, 310.
[6] H. Kayser: Chem. News, **72**, 89.
[7] Proc. Roy. Soc., **59**, 60; Chem. News, **72**, 295.

In a recent paper[1] it is stated that a zirconiferous sand, containing uranium, and yielding an "abundant" supply of helium, is found in large deposits on the coast of Brazil.

Finally, attention may be drawn to a paper on "Argon and Helium" in the number of the *Edinburgh Review* for October, 1895. Written—of course anonymously—in what is called a "popular" style, this article does not altogether fail to be amusing even if at times not instructive. The effort to overbalance the conclusion of the scientific world upon certain personal questions by the use of an extravagant metaphor or a sneering phrase, would be exasperating if it had to be taken seriously. W. W. R.

Two Recent Publications upon Carbohydrates.

The amount of pure research and noteworthy attainment in the field of the carbohydrates during the past ten years has probably equalled that in any other branch of organic chemistry. Some of this research may justly be regarded as classic, notably the series of difficult syntheses of the monosaccharides by E. Fischer, and the confirmation thereby, in the most conclusive manner yet recorded, of the theoretical principles underlying stereochemistry. Less prominent but hardly less important are the numerous fundamental reactions which have been discovered and developed, and which have served as the most indispensable agents contributing to the success of investigators. Such are the methods for oxidation and reduction used by Fischer, his development of the phenylhydrazine reactions, and his methods of transforming the stereoisomeric acids into each other; Kiliani's method for increasing the number of carbon atoms in a sugar by the addition of hydrocyanic acid, and Wohl's successful "Abbau" of hexoses to pentoses through the glycosoxime; the application of Raoult's method to the determination of the molecular weights of the carbohydrates, etc. Explorative research has added new carbohydrates to those already known to occur in nature, chief among which are those of pentatomic character. These and many other minor discoveries have served wholly to revolutionize the former views regarding carbohydrates. At one time hardly considered worthy of attention by pure scientists, these bodies now serve to demonstrate some of the most important chemical theories. At the present time the interest in carbohydrates, while not less from the practical standpoint, has largely grown on the side of theoretical and pure chemistry. One immediate effect of this is the necessity

[1] H. Wilde: Phil. Mag., 40, 468.

for revision of text-books and a demand for new and modern treatises. Two works of this kind have opportunely appeared during the year and those interested in this subject have reason to rejoice that they are from the hands of two men of such experience and knowledge in this special field as Professor Tollens and Dr. von Lippmann, both of whom have formerly published leading works on this subject.

These recent books leave little or nothing to be desired, the one offering a comprehensive review of the entire class of carbohydrates, and the other a highly specialized monograph upon the sugars. No fact or discussion of any importance bearing upon the subjects has been omitted from these works, and they bring within the reach of the student and investigator the substance of the diffused and scattered literature on the carbohydrates, revised and classified by the two persons best fitted for the task. The two works are in no sense duplicates of each other, and both are indispensable to one who would acquire command of the subject or have at hand accurate references.

KURZES HANDBUCH DER KOHLENHYDRATE. VON DR. B. TOLLENS, Professor der Chemie an der Universität, Göttingen. Zweiter Band enthaltend die Forschungsergebnisse der Jahre 1888–1895. Breslau. Verlag von Eduard Trewendt. 1895. pp. 407.

When the first edition of the Handbuch appeared, in 1888, it was rightly regarded as the most valuable work upon the subject existing. The great extension of knowledge in this field since then necessitates a quite new and modified view of the carbohydrates which this second edition admirably supplies. The former heterogeneous group of substances included under the name carbohydrates has now undergone such revision and investigation that a more or less complete systematic classification is possible. Many of these bodies are found to be members of an extended homologous series of chemical bodies of similar constitution, while others of less evident theoretical relationship are nevertheless undoubtedly connected with the better identified members of the family. The study of these bodies from the standpoint of pure chemistry has become attractive and productive of important results. This work, therefore, properly devotes much of its space to a discussion of the purely chemical characteristics of the carbohydrates, and to recording the results of the latest investigation in this line. Some of the more technical features of the first edition have been omitted, but not in a way to lessen the value of the work in any sense.

A concise definition of a carbohydrate is not ventured by the author, although one of less experience might have so committed himself. He no longer limits the term to those compounds containing six atoms of carbon, as in the earlier edition, but extends the term over the series containing from four to nine carbon atoms and possessing the other well known properties of sugars. For these simple monosaccharides, which all reduce alkaline copper solution, the general name "glycose" is suggested, the distinction being made between this class and "glucose" or grape sugar. Other sugars are included in the divisions of di- and tri-saccharides, while the amorphous carbohydrates of evident close relationship are included under the general term polysaccharides. Other related bodies such as the higher alcohols and the acids derived from the sugars by oxidation, are all considered in due place, so that every substance showing any relation to, or derivation from, the true carbohydrates receives attention. The greater portion of the work is devoted to the descriptions of the individual bodies, including their reactions, occurrence, recognition, etc. Even those bodies of doubtful place and character are not excluded. This comprehensive feature is especially valuable to the investigator, supplying as it does all available information in each case. References to original publications are given in great number. This arrangement of these references in a body at the end of the work is not the most convenient, but is compensated for by the absence from the text of the confusing parenthetical references.

The discussion of the constitution of the carbohydrates is very full and satisfactory. The author himself is an advocate of the ethylene-oxide structure for dextrose, but gives with equal detail all of the arguments for the aldehyde structure, and suggests at the close the probability that different substances exist having the same composition, of which the one may have the aldehyde and the other the ethylene-oxide formula. The configuration of the different sugars according to the theory of stereoisomerism is fully illustrated by graphic formulas. The synthetic processes employed by Fischer are also fully described.

The work is the only one of its kind in existence and is an indispensable guide and reference book to both student and investigator.

DIE CHEMIE DER ZUCKERARTEN. VON DR. EDMUND O. VON LIPPMANN. Director der Zucker-Raffinerie zu Halle. Zweite völlig umgearbeitete Auflage der vom Vereine für die Rübenzucker-Industrie des Deutschen Reiches mit dem ersten Preise gekrönten Schrift. Die Zuckerarten und Ihre Derivate. Braunschweig. Friedrich Vieweg und Sohn. 1895. pp. 1174.

As the outcome of a prize monograph upon sugars, presented in 1878 by Dr. von Lippmann, the author published in 1882 a modest work entitled "Die Zuckerarten und ihre Derivate" of which the present treatise is hardly a second edition but rather a new work with a new title. It treats, as the name indicates, of sugars only, other related carbohydrates being ignored. The author abides strictly by a rational classification on a structural basis, which is more easily done than if the entire group of carbohydrates were under consideration. All sugars are classified as mono-, di- or trisaccharides, typified respectively by glucose, sucrose, and raffinose. Properly enough, no distinction is made in treatment between the natural and artificial sugars. Beginning with glycolic aldehyde, $C_2H_4O_2$, each member of the homologous series is discussed with great detail up to and including the *a*-manno-nonose, $C_9H_{18}O_9$. The cyclic compounds, such as quercite, chinite, inosite, etc., are also described, although not strictly sugars. The plan of the work is to give a complete resumé of all that is known about each sugar, including references to original papers with the names of investigators. For each sugar the systematic order of treatment is as follows: Occurrence, preparation, and formula; 2. Physical properties; 3. Behavior toward heat; 4. Behavior towards reagents; 5. Fermentation; 6. Compounds and derivatives; 7. Recognition and estimation.

A close examination of the work reveals a painstaking thoroughness and completeness of treatment deserving of unqualified admiration. The great number of references shows a complete familiarity with the literature of the subject, of which the author has already given evidence in his "Geschichte des Zuckers." No fact is considered of too little importance to be given a place, although the mass of material has been so carefully edited that one feels that each reference has been given its proper emphasis. This method of treatment, when applied to some of the more important sugars, yields an exhaustive monograph in itself. For instance, the discussion of dextrose occupies 240 pages, while some forty pages more are given to invert sugar. The subject of sucrose covers over 250 pages, and so on. There are special chapters on the constitution, configuration and synthesis of sugars, the

origin of sugar in plants, their physiological importance, etc., in which the results of all the most important recent investigations find place. Even many publications appearing after the work went to press, have been carefully abstracted and the abstracts added in a supplementary part, and the whole is indexed for authors and subjects separately with great minuteness. The work of preparing such a treatise is great, and the result is wholly satisfactory, easily surpassing all other works in its particular field. W. E. STONE.

OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN. No. 63. ZUR ENTDECKUNG DES ELEKTROMAGNETISMUS. 33 pp., price 1.40 marks; No. 66. DIE ANFAENGE DES NATÜRLICHEN SYSTEMES DER CHEMISCHEN ELEMENTE, 34 pp., 0.60 mark. Leipsic. W. Engelmann, 1895.

Two of the most recent numbers of Ostwald's collection of scientific classics[1] are reprints of chemical papers. One of them contains the researches of Oersted (1820) and of Seebeck (1821) on electromagnetism (its discovery) and the "Magnetism of the Galvanic Cell," with editorial comments by von Oettingen; and the other is made up of the papers by Doebereiner (1829) and Pettenkofer (1850) on the arrangement of the chemical elements in triads, the scheme which ripened in the discovery of the periodic law. The latter collection is edited with great care by Lothar Meyer, and is concluded by a new paper by him on "The further development of the systemization attempted by Doebereiner and Pettenkofer." The importance of these convenient and inexpensive little books needs no comment. J. E. T.

DIE LEHRE VON DER ELEKTRIZITAET. By G. WIEDEMANN. Second (rewritten) edition, volume iii. Large 8vo. 1139 pp. Braunschweig: Vieweg, 1895. Price, 28 marks.

Comment has already been made in this Journal[2] upon the appearance of the first and second volumes of Wiedemann's great book on electricity. The third volume of this remarkable and authoritative work is now before us; it treats electrodynamics and electromagnetism, and its most prominent characteristics are those of the foregoing volumes—a comprehensive mass of material and the always attractive historical-critical method. The subjects treated would seem to have little to do with any forms of chemical action, and the volume will certainly interest the chemist less upon the whole than the preceding second volume which is devoted to electrochemistry, yet the present number is not devoid of chemical inter-

[1] See this Journal, p. 17, 629. [2] This Journal, 15, 606; 16, 563.

est. We find, for example, studies on the influence of magnetization upon reactions which involve salts of iron, or upon the readiness with which metallic iron dissolves in solutions of salts and acids; there appears a full account of work done upon the electromotive forces of the electrolytic currents which arise between magnetized and unmagnetized electrodes, and upon the similar currents observable when diamagnetic bismuth electrodes are employed; and we note an interesting application of thermodynamic theory made by Pellat in the endeavor to account for the experiments of Remsen.

The mechanical execution of the work is excellent and the material presented is brought thoroughly down to date. Its scope may be inferred from the fact that the volumes now issued include nearly thirty-four hundred closely printed large octavo pages. J. E. T.

PHYSIKALISCH-CHEMISCHE PROPAEDEUTIK. By H. GRIESBACH. Large 8vo. First half, 272 pp. Leipsic, W. Engelman, 1895. Price six marks.

The *Propaedeutik* of Griesbach is a rather impressive mixture of many things. It is intended to serve as an introductory text book on physical chemistry, for the use of students of chemistry and of medicine. The office of its first half is apparently to supply an introductory store of philosophical, astronomical, historical, biographical, etymological, and biological information, leaving the reader to hope that the second half—soon to appear—may contain some details more immediately concerning physical chemistry.

The book begins with a disquisition upon philosophy in general, and Greek philosophy in particular. Measurement and measuring instruments are then taken up in great detail, ordinary dividers and the coördinate paper used for drawing curves being, for example, minutely described, and these things are followed by a lecture on matter. The discussion of matter leads our author easily and naturally, by way of the nebular hypothesis and the experiments of Plateau upon capillarity, to the doctrine of energy; and here we meet the assertion that energy, being a constituent of substance, must itself be an independent entity. Now this is simply ridiculous, and in fact this failure to regard energies as work-equivalents whose analytical forms depend upon the definition of work leads at once (p. 105) to the absurd conclusion that the conception of work is *derived* from the idea of energy.

We are next conducted through a number of chapters on such things as velocity, circular motion, friction, the constitution of matter and of ether, and thirty-seven pages of the

history of ideas concerning atoms; all this leading up to a not unpretentious treatise on biology. Deep water appears here, for we are instructed in cell biology, ferments, and infectious diseases, phases of physical chemistry into which the attainments of the present writer unfortunately do not extend.

There appears throughout the text a multitude of biographical sketches of philosophers, mathematicians, physicists, chemists, etc., to whose work or ideas reference is made; and also a great mass of material concerning the etymology of the terms employed. And the whole is enlivened by occasional quotations from Latin poets—especially Ovid. Some of the biography and anecdote is interesting, some amusing, and all presumably authentic, but still one does not seek information of this kind in an introductory text-book on physical chemistry. And all the etymological Greek, Latin and Arabic is interesting enough in its place, but its place would seem to be a dictionary or other philological work rather than a treatise on physical science. The author has, in brief, collected a lot of things which it is desirable to know, but which do not necessarily belong together, and which owe their connection with physical chemistry solely to the fact that everything seems to be in some wise related to everything else. The book is certainly an industrious compilation, but it is a compilation of essentially heterogeneous materials, and where the physical chemistry comes in is not as yet easily seen.

J. E. T.

A Laboratory Manual of Organic Chemistry. A Compendium of Laboratory Methods for the Use of Chemists, Physicians and Pharmacists. By Dr. Lassar-Cohn, Professor of Chemistry in the University of Königsberg. Translated, with the Author's Sanction, from the Second German Edition, by Alexander Smith, B.Sc. Ph.D., Assistant Professor of General Chemistry, in the University Chicago. London and New York: Macmillan & Co. 1895. 8 vo. pp. 403. Price, $2.25.

This book has already gone through two editions in the original German, and a French translation has appeared, all in the short space of three years. These facts speak well for the value placed on the book by chemists, and make it probable that the present English translation will meet with a warm welcome from all workers in the field of organic chemistry, both in this country and in England.

It covers a field not previously occupied by any of the numerous text-books and laboratory manuals on organic chemistry, and is exactly what its title claims it to be; a compendium of the methods actually employed in the laboratory of organic chemistry. The attempt has been made to bring

together here the methods which may be used in carrying out all the common operations of organic chemistry without reference to the particular substance employed, though many examples are given to show how various investigators have overcome difficulties in particular cases.

The book is one that should be in every laboratory in which work in organic chemistry is carried on. It cannot fail to be of value to both teachers and students of this very important branch of the science of chemistry. On every page will be found valuable suggestions culled from long experience in the practice of organic chemistry, and hidden away in the great mass of literature on this subject, and therefore practically inaccessible to the average student.

The author very modestly states in his preface to the first German edition of the book, that "Its object will have been attained if the book encourages work in the field of organic chemistry and lightens the labor of the workers." That this object has been accomplished will be gratefully acknowledged by those who have had occasion to use the book.

The translation is well done, and the author is to be congratulated that the translator is an experienced worker in the field which the book covers. The print is excellent, and the same may be said of the illustrations and the flexible binding. Altogether the book is one which does credit to both the translator and the publishers. W. R. O.

JAHRBUCH DER ELEKTROCHEMIE. Berichte über die Forschritte des Jahres, 1894. Im wissenschaftlichen Theile bearbeitet von Dr. W. Nernst, Professor an der Universität Göttingen, Direktor des Instituts für physikalische Chemie und Elektrochemie. Im technischen Theile bearbeitet von Dr. W. Borschers, Lehrer an der Kgl. Maschinenbau und Hüttenschule zu Duisburg. I Jahrgang. Wilhelm Knapp. Halle a. S., 1895. pp. 274.

As the Jahrbuch der Chemie furnishes brief abstracts of the work done in the entire field of chemistry during the year for which it purports to be a record, so the Jahrbuch der Elektrochemie gives an account of the advances made in electrochemistry for any given year. The first volume, which appeared about the middle of this year, reviews the work published in 1894.

The chapters on physical chemistry, in the Jahrbuch der Chemie, are written by Nernst and Küster. The scientific electrochemistry in the Jahrbuch der Elektrochemie is written by Nernst. That part of the former, which has to do with electrochemistry is reprinted in the latter, but this is greatly enlarged and supplemented. We find, in the scientific part

of the Jahrbuch der Elektrochemie an account of the recent work on Solution of Solids; Electrolytic Dissociation; Electrolytic Conduction of the Current; The Dilution Law; Dissociation of Water; Potential Differences between Solutions; Potential Differences between Metal and Solution; Anomalous Potential Differences; and on Electrodes of the second kind.

The applied electrochemistry is discussed extensively by Borchers, with the aid of a large number of illustrations of apparatus. Among the subjects treated are; Accumulators; Electro-thermal Apparatus and Methods; Deposition of the Metals and Non-Metals; The Alkali and Chlorine industry, etc.

About one-fourth of the volume is devoted to the scientific side, the remainder to the applied. The electro-chemist will thus be provided, yearly, with an account of the most recent work done in his field. H. C. J.

ANLEITUNG ZUR MOLEKULARGEWICHTSBESTIMMUNG, NACH DER "BECKMANNSCHEN" GEFRIER-UND SIEDEPUNKTS-METHODE. Von DR. GOTTHOLD FUCHS, Assistent am Laboratorium für angewandte Chemie, Erlangen. With 18 wood-cuts. Wilhelm Engelmann. Leipzig, 1895. pp. 41.

This little book gives an account of the Beckmann freezing-point and boiling-point methods, for determining the molecular weight of substances in solution, together with a sufficient number of illustrations to make clear the discussion of the forms of apparatus, which Beckmann has devised for carrying out these methods.

The instruction is not purely mechanical, the theoretical significance of the results being treated fully enough to give the reader an intelligible view of the fundamental ideas on which these methods are based.

The value of the book would, however, have been enhanced by treating, not only of the "Beckmann methods," but of the freezing- and boiling-point methods in general, as applied to the determination of molecular weights. Thus the boiling-point method of Beckmann has been very greatly improved as a method for determining molecular weights by Hite,[1] whose apparatus is preferable to any form ever suggested by Beckmann, enabling one to determine *more accurately* the boiling-point of a low-boiling solvent, or of a solution.

On page 8, there is an error, which is of special interest to the writer of this notice. We are told that "recently a

[1] This JOURNAL, 17, 507.

thermometer, divided into $\frac{1}{1000}°$ has been constructed, and applied by *Meyer Wildermann* and his scholars, in scientific investigations." The writer wishes to state that *he employed, first*, a thermometer answering the above description in the laboratory of Ostwald, in which Wildermann was working. The thermometer, which Götze constructed, at the suggestion of Ostwald, the apparatus and method of work were observed by Wildermann, who, about *a year later*, obtained a similar instrument and began his work in England. The facts speak for themselves.[1] H. C. J.

EINFÜHRUNG IN DIE MATHEMATISCHE BEHANDLUNG DER NATURWISSENSCHAFTEN. Kurzgefasstes Lehrbuch der Differential und Integralrechnung mit besonderer Berücksichtigung der Chemie. Von W. Nernst, Professor of Physical Chemistry in the University of Göttingen, and A. Schönflies, Professor of Mathematics in the University of Göttingen. With 61 figures in the text. München and Leipzig: Dr. E. Wolff. 1895. pp. 309.

The object of this book is in the words of the authors, "to aid students, who are in the earlier stages of scientific work, in the study of the higher mathematics." The average textbook on the calculus naturally deals with the subject from the standpoint of the mathematician, and from it one may learn to differentiate and integrate with facility, without seeing in many cases, the full significance of these processes, in their applications to the experimental sciences. The authors having this in mind, have pointed out the physical significance of the mathematical expressions in some cases. After the paragraph on the differential coefficient, we find the next on its physical significance. Another paragraph deals with the geometrical and physical significance of integration constants, etc.

The book has twelve chapters, treating of: The Elements of Analytical Geometry; the Fundamental Conceptions of the Differential Calculus; the Differentiation of Simple Functions; the Integral Calculus; Applications of the Integral Calculus; Definite Integrals; the Higher Differential Coefficients and the Functions of Several Variables; the Infinite Series and Taylor's Theorem; the Theory of Maxima and Minima; the Evolution of Numerical Equations; the Differentiation and Integration of Functions, Empirically Determined; and Examples from Mechanics and Thermodymamics.

To the mathematician or the mathematical physicist this work contains much, that will appear to be very elementary, and that is easily accessible in the many texts on the

[1] See *Zeitschrift für Physikalische Chemie*, **11**, 110, and 529; and **12**, 623.

calculus already existing. It must, however, be remembered that this treatise was not prepared for such, but for those who are not thoroughly versed in mathematics. To these the elementary character of this book will not be objectionable.

H. C. J.

ELEMENTS OF MODERN CHEMISTRY. BY CHARLES ADOLPHE WURTZ. Fifth American Edition. Revised and Enlarged by WM. H. GREENE, M.D., and HARRY F. KELLER, PH.D. (Strasburg). With a portrait of the author and numerous illustrations. Philadelphia: J. B. Lippincott Company. London: 10 Henrietta Street, Covent Garden. 1895. Pp. 808 + 16.

When the first French edition of this book appeared in 1868, the expression "Modern Chemistry" had an important meaning. It meant a change in the system of atomic weights employed, and a complete cutting loose from the dualistic conception of compounds that even up to that time prevailed among all except the younger chemists. To-day the term needs to be explained, and it is unfortunate to see it in the title of a book just published. As regards the book itself, every one who knows anything about chemistry knows that Wurtz was a master, that he was one of those who contributed largely to the development of "Modern Chemistry." His book was always highly esteemed.

This is the fifth American edition. In its preparation "the aim has been to preserve as nearly as possible the original plan and character of the work, but at the same time to make such changes as will entitle it to continue to rank as a truly modern text-book." In spite of the efforts of the revisers, there is abundant evidence that the book is old. The classification of the compounds of carbon is to be mentioned first in this connection. No one now-a-days would begin a work on organic chemistry with the cyanogen compounds, and then lead the student through the intricacies of the cyanides, the ferrocyanides and ferricyanides, cyanic acid, cyanuric acid, urea, biuret, etc., before presenting some of the simpler compounds, the relations between which can easily be traced. It is to be hoped that, when another edition is called for, the revisers will adopt the "modern" classification.

Stereoisomerism is not clearly explained, because too briefly. Would it not be better to make the relation between the three varieties of lactic acid the basis for the explanation, and then show how an extension of the same ideas enables us to explain the relations between the four varieties of tartaric acid, instead of using these latter relations as the basis of the explanation?

A result of the older method of classification is to bring

together aconitic acid, a tribasic acid, and itaconic, citraconic and mesaconic acids, which are dibasic. Why? Because they are all formed from citric acid, either directly or indirectly, by heat. Hence the sub-heading "Pyrogenous Acids derived from Citric Acid," (p. 623), which certainly has an antique flavor. Again, the treatment of glucosides under sugars, and before the aromatic compounds have been studied, is not logical, as it requires premature reference to such compounds as benzoic aldehyde, benzoic acid, saligenol, salicin, phloretin, gallic acid, etc.

In discussing the constitution of benzene, the revisers give the preference to the centric formula proposed by Armstrong, and afterwards again brought forward by Baeyer, and the impression is left upon the mind of the reader that Baeyer himself prefers this formula. This, however, is not correct, as, according to the last communication of Baeyer on this subject, he has concluded that the Claus formula is more in accordance with the facts. It is, however, true that Bamberger still uses the centric formula in dealing with the facts presented by naphthalene.

While this book, like other books, is not perfect, it is on the whole a trustworthy guide to chemistry. It appears, however, to contain too much for beginners and not enough for the advanced student. I. R.

NOTES.

The Water of Crystallization of Barium Picrate.

In the year 1841 Dumas[1] mentions this substance and says that the analyses made by Liebig show it to consist of "1 atom of baryta, 1 atom of picric acid and 6 atoms of water." He makes, however, no reference to any other publication by Liebig.

In the same year Marchand[2] gives an accurate description of the same substance: its physical properties and methods of preparation.

He assigns to the compound the (modernized) formula

$$Ba[C_6H_2(NO_2)_3O]_2 + 5H_2O.$$

In 1875, Post and Mehrtens[3] determined the solubility and

[1] Ann. Chem. (Liebig), **30**, 354.
[2] J. C. Prakt. Chem., **25**, 363. Ann. Chemie (Liebig), **32**, 345.
[3] Ber. d. chem Ges., **8**, 1552.

specific gravity of these crystals and to them assigned (without giving reasons or analytical data) the formula

$$Ba[C_6H_2(NO_2)_3O]_2 + 4H_2O.$$

Finally, in 1885, Tscheltzow,[4] who was engaged in thermochemical study of this compound makes use (without giving reasons or analytical data) of the formula

$$Ba[C_6H_2(NO_2)_3O]_2 + 6H_2O.$$

In connection with some work done in this laboratory it has been necessary to determine definitely the number of molecules of water contained in the crystals. Barium picrate was prepared by treating picric acid with an excess of barium carbonate, filtering the hot solution, from which the crystals separate on cooling. To free from adhering moisture, the crystals were at times simply pressed between filter-paper. (This is the case with Nos. 3 and 5). Again the substance was also dried by exposure to the air for a day. (The substances thus prepared were 1, 2 and 4.)

1. 2.0530 gram barium picrate yielded 0.6803 gram $BaSO_4$.
2. One-fourth of 1.1556 gram of substance yielded 0.0963 gram $BaSO_4$.
3. 0.9977 gram substance yielded 0.3334 gram $BaSO_4$.
4. 1.1160 gram substance yielded 0.4720 gram $BaSO_4$.
5. 0.5002 gram substance yielded 0.1672 gram $BaSO_4$.

Percentage of Barium found.

1	19.57
2	19.58
3	19.65
4	16.59
5	19.64
	19.61

Theoretical for $BaP_2 + 5H_2O$ 20.07 per cent.
" " $BaP_2 + 6H_2O$ 19.55 "

It would seem certain that the specimens which I have analyzed must have contained six molecules of water. In this connection however, the results of Marchand (loc. cit.) are of importance and interest. His results (recalculated by me) show 19.96 and 20.01 per cent. of barium. These figures evidently indicate a salt containing only five molecules of water.

[4] Comptes rendus, **101**, 381.

Further investigation will be made to determine under what conditions these hydrates can be formed, or to determine whether one exists—that with six molecules of water.

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WORCESTER, MASS., NOV. 27, 1895.

The Berichte, "Beilstein," and the Centralblatt.

According to a recent circular, issued by the German Chemical Society, the society proposes to undertake the preparation and publication of the future editions of Beilstein's "*Handbuch der Organischen Chemie*," and of the "*Chemisches Centralblatt*," and to give up the publication of the *Referate* as a part of the *Berichte*. There can hardly be two opinions in regard to the wisdom of this plan, provided always that the preparation of the abstracts for the new Centralblatt is to be well done, and of this there can be little doubt. The *Referate* have never been satisfactory to any one, owing largely to a lack of money. The Centralblatt has in general well served the purpose for which it is prepared and, as it is understood that the present editor will remain in charge, it is probable that it will be even better in the future. All must feel thankful that the apparent growth of the *Berichte* is to be checked, and that the separate volumes may hereafter be less like cubes, and more of the order of irregular parallelopipeds.

As regards the Handbuch, there is but one who can do its work, and that is Beilstein the Great. No one can worthily succeed him. Others may try their hand at the work, but we cannot expect them to reach the high standard that Beilstein has set. While, therefore, we must recognize the wisdom of the plan proposed by the society, we cannot avoid a strong feeling of regret that the "Beilstein," so familiar, so dear, and so useful to all of us, is not to be "Beilstein" in the future, whatever else it may be. I. R.